Medals. The Redwood Medal is awarded, at the discretion of the Council, to the person who shall have made the most meritorious contribution to petroleum technology, in the form of a paper or papers published in the Journal of the Institution, during two successive sessions, preference being given to original work and to papers which have been read before the Institution and discussed. The award is not confined to members of the Institution and may be withheld if no contribution is considered to be of sufficient merit.

A medal and a prize of five guineas is awarded annually by the Council to that Student Member of the Institution who shall, in their opinion, have presented the best paper during the session.

Research Fellowship. The sum of £300 is allocated in each calendar year to a Fellowship for Research in technical and scientific problems which have a direct bearing on the Petroleum Industry. Additional grants, to a limit of £50 per annum, may also be made towards expenses.

The Fellowship is tenable for one year at an institution or in works approved by the Council, and may be renewed for a second year at the discretion of the Council.

Applicants, other than members of the Institution, must be of British nationality and must hold an Honours Degree in Science or an approved equivalent.

Applicants for the Fellowship must be in the hands of the Secretary of the Institution not later than June 1st of each year, and the necessary form, together with full particulars, can be obtained from him at Aldine House, Bedford Street, London, W.C. 2.

Advertisements. Advertisements are inserted in the Journal, and information as to terms, etc., can be obtained from Mr. Thomas Tofts, 301-302, Bank Chambers, 329, High Holborn, W.C. 1. (Telephone No. Hol. 4776.)

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Benevolent Fund. The Benevolent Fund is intended to aid necessitous persons who are or have been members of the Institution, and their dependent relatives.

The Fund is raised by voluntary annual subscriptions, donations, and bequests, and all contributions should be sent to the Secretary of the Institution at Aldine House, Bedford Street, London, W.C. 2. The Fund is administered by the Council through the Benevolent Fund Committee, and all applications in connection therewith must be made on a special form which can be obtained from the Secretary of the Institution.

Appointments Register. A register of members requiring appointments is kept at the office of the Institution for the convenience of firms requiring the services of petroleum technologists, etc., it being understood that the Institution accepts no responsibility and gives no guarantee.

Library. The Institution's Library may be consulted between the hours of 11 a.m. and 4 p.m. daily. (Saturdays, 11 a.m. to 12 noon.)

PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Mr. L. H. Appleby has left for Persia.

Mr. F. H. Garner has returned to New York.

Mr. J. Fenton is home from Persia.

Major T. R. H. Garrett is in Rumania for a short period.

Mr. R. Harman has left Burma and is in Rumania.

Mr. J. B. Kay is home from Venezuela.

Mr. W. E. Madden has left Mexico and is in Holland.

Mr. Launcelot Owen is returning home from Venezuela, *via* Colombia and Spain, and expects to be in London before the end of May.

Mr. J. S. Pirie has returned from Burma.

Mr. J. W. Reid is home from Persia.

Mr. E. K. Sargison has left for Burma.

Dr. R. Schider has left for Burma.

Mr. J. G. Smillie is in Spain.

Mr. W. C. Sydenham has left for Persia.

The Secretary will be glad to receive information as to the whereabouts of the following members :—C. A. Bauduin, J. C. Fortune, W. J. Harris, L. B. Holloway, W. Johnston, A. F. C. Parker, L. R. Phillips and F. E. G. Watson.

OBITUARY.

JAMES BRYSON, J.P.

It is with deep regret that we have to record the death of Mr. James Bryson, J.P., which took place on January 19, 1930, at his residence, Ballengiech, Pumpherston.

Mr. Bryson, who was in his 77th year, became indisposed about the middle of October. Hope, however, was entertained of his

recovery but, towards the end of December, his illness assumed a critical phase and he gradually sank.

Born in Coatbridge, he received the usual education at a local school and served his apprenticeship as an engineer with the Vulcan Iron Co. He gained experience afterwards with Scott's Shipbuilding and Engineering Co., Greenock; the Carron Iron Co., and the Gartsherrie Iron Co. He was essentially a "self-taught," as he became a "self-made" man.

Mr. Bryson was actively engaged in the Scottish Shale Oil Industry for the long period of forty-three years. Coming as Works Manager of the newly launched Pumpherston Oil Company in 1887, he devoted all his energies to the development and improve-

ment of the plant and process, so far as was possible during these first critical and trying years of the existence of the youthful company, consistently with the economy necessary to preserve the comparatively small capital expenditure which, in later years, and under more favourable market conditions was to prove a very valuable asset and a fundamental factor in the future success of the company. In this way he was largely instrumental in promoting the enlightened policy of the founder of the Pumpherston Company, the late Mr. William Fraser.

When the operations of the Company were gradually extended by the acquisition of new shale fields, it devolved on Mr. Bryson to prepare plans for and to carry out the erection of new crude works, for the production of Crude Oil and Sulphate of Ammonia from the shale mined in the new areas, at Seafield, Livingston Station and Tarbrax, in the chronological order stated. In these days, previous to the introduction of motor traffic, the difficulty and discomfort and expenditure of time incurred in supervising this work of construction at distances of from six to sixteen miles may be readily imagined, and when it is realised that during all this period of expansion, Mr. Bryson was at the same time responsible for the management of all these four large works, first in succession as completed, and ultimately and for many years simultaneously, it will be seen that only one endowed with very exceptional physical and mental powers could have so successfully sustained the burden and fulfilled the task. Moreover, it was no mere superficial general supervision that he ever gave either to the designing and erection of the new works or to their administration. No detail was apparently too trivial to be overlooked; all was carefully considered and appraised, yet their due measure of importance was attached to each undertaking: and the untiring energy, quick insight, and patience in the mastery of new detail, which characterised his work, all contributed to equip him with a technical knowledge and experience of the manufacturing plant and process unrivalled in the industry.

The introduction of the "Pumpherston" or "Bryson" Retorts into all the Company's works, and into some of the shale oil works, effected such striking economies that the cost of retorting the shale was halved at one stroke, and may truly be said to have ensured, at a critical period in its fortunes, the future success of the Pumpherston Oil Company, which for many years continued to maintain a high level of financial prosperity.

In 1910, he was a made a Director of Pumpherston Oil Company, and five years later was appointed Joint-Managing Director.

When, in 1919, the Shale Oil Companies in Scotland were amalgamated as Scottish Oils, Ltd., Mr. Bryson became General Works

Manager, and entered upon a new phase of work—the refining of crude petroleum. The first duties devolving upon him were the designing and erection of a very large new petroleum refinery at Grangemouth; the adaptation of existing and the installation of new plant at Uphall to enable this former shale oil works to deal with the refining of petroleum; and the erection of up-to-date workshops, etc., at Middleton Hall. In this work he enjoyed the co-operation of the late Mr. A. C. Thomson, Chief Constructional Engineer to Scottish Oils Ltd., with whom Mr. Bryson maintained a very close relationship and warm and loyal friendship for a very long period of years. In 1928, he became a Director in Scottish Oils, Limited.

He became a Member of the Institution of Petroleum Technologists in 1920.

Despite his business responsibilities, Mr. Bryson took an active part in the public life of the community. He was keenly interested in the development of education, and for about 35 years his influence and administrative ability were ungrudgingly given as a member of Mid-Calder School Board. He was a Justice of the Peace for Midlothian; chairman of the Calder District Committee of Midlothian County Council; chairman of the Midlothian Advisory Committee for the appointment of Justices of the Peace; and vice-chairman of Midlothian Health Insurance Committee.

The funeral took place on the following Wednesday, at Mid-Calder Cemetery, and there was a very large concourse of mourners, the Institution of Petroleum Technologists being represented by the President, Dr. A. E. Dunstan. The Service, in the house, was taken by the Rev. W. R. Scott, Rev. J. M. Jeffrey and the Rev. John Lindsay, while in Bridgend church, simultaneously, a short service was conducted by the Rev. W. W. Clark, Rev. Chas. Allen and the Rev. G. Gilmour, the large audience that filled the church testifying to the high place the departed chief held in the affections and esteem of those amongst whom he lived and worked. The Rev. J. M. Jeffrey officiated at the graveside.

NOMINATIONS FOR MEMBERSHIP OF THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The following have been nominated for membership of the Institution of Petroleum Technologists and their Application Forms may be seen at the Offices of the Institution:—

As Members.—Douglas Leonard Alexander, Eric James Dunstan.
As Associate Members.—William Duff, Edward Vernon Wharton.
Transfer to Associate Member.—Hendrik Willem Slotboom.
As Students.—Jack William Clack, Samuel Elliman, Kenneth Byrne Lanyon;

HEALTH IN THE TROPICS.

Courses of lectures on Tropical Hygiene for those, outside the medical profession, who are taking up life in the tropics are given at regular intervals at the London School of Hygiene and Tropical Medicine. Full particulars can be obtained from the Secretary at Keppel Street, Gower Street, London, S.W. 1.

In the course of an introductory lecture on February 26, 1930, the director, Sir Andrew Balfour, emphasised the importance of the would-be resident in the tropics knowing how to take care of himself and avoid infection. Much knowledge of tropical diseases has been gained during the past thirty-five years and, the courses gives at the School are designed to give the layman information calculated to be of interest and benefit to him.

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THE PETROLEUM INDUSTRY.

A brief survey of the Technology of Petroleum based upon a Course of Lectures given by Members of the Institution of Petroleum Technologists at the Petroleum Exhibition, Crystal Palace, 1920.

This work will be found of value to students and those desirous of obtaining an elementary knowledge of the Technology of Petroleum.

A few remaining copies for disposal at **2s. 6d.**

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No. 80. Vol. 16.

REPORTS ON THE PROGRESS OF NAPHTHOLOGY, 1928—1929.

Petroleum Geology.*

By V. C. Illing (Member).

At intervals along the path of progress it is a good thing to look back. In a subject like geology, where theory plays such an important part in all advance of knowledge, the vista of the road travelled is strewn with discarded ideas and mile-stoned with ascertained facts. This exercise is a healthy encouragement to further effort, and, rightly conceived, its lessons may be of use in correcting errors before they become too deeply rooted in our literature. Petroleum geology is growing at an ever-increasing rate, and, like the circle of ripples on water disturbed by a falling stone, its widening activities take in all angles of thought and every branch of knowledge that may bring data to the geologists. The science needs not only its geologists but its physicists, chemists, petrologists, palæontologists and geophysicists, all specialists in certain aspects of the problems of petroleum which require detailed knowledge or specialised skill. Around each of these branches has grown in recent years a special literature. We have production geology, with its study of gas conservation, repressuring, water flush, estimation of reserves, and that bugbear of deep drilling, "crooked holes," etc. These are not subjects in a geologist's normal equipment, but they are of first importance to a geologist resident in a producing field. The waters above, within, and below the oil measures require careful analysis and study. The chemist and geologist here collaborate to produce results of value to the geologist and engineer. The samples from the wells need intensive study by the petrologist and palæontologist, while the field geologist faced with potentially valuable areas with no rock exposure, or with other problems where normal attack fails, calls to his aid the results of the geophysicist to give him data for theoretical conclusions. Few of these methods are peculiar to petroleum geology—but the combined association of them all renders the subject too varied and extensive to lend itself to a simple critical review. From small beginnings petroleum geology has grown until at the moment it is probably the greatest single economic outlet for the science of geology. It has its own scientific societies and research institutions,

* Paper received, Jan. 4, 1930.

and is making progress along certain directions of geological study, which had not received adequate attention hitherto. The testing of surface structures at depth has brought home to the geologist what ought to have been self-evident. The map is not the final test, the model or three-dimensional conception is the only real test of the accurate delineation of structure. Geology has been hampered for long, and is still hampered by the failure to realise the fundamental error of representing structures with different horizontal and vertical scales; the results are mere caricatures. Petroleum geology has done much to eliminate this mischievous practice. Further, the intensive study of sediments is being greatly fostered by this branch of geological work. One service above all others is being rendered by petroleum geology. The collection of a great bulk of physical, chemical and structural data with regard to the earth's crust at depth, and the drawing closer of the bonds which link the sister sciences.

Dealing first with the broad tendencies of the last two years rather than with individual achievements, there is a distinct tendency to deal with some of the problems on more rational lines. The discussion of areal geology ceases to be a mere catalogue of rocks and structures and becomes an attempt to visualise the successive geological events in terms of environment, sedimentation, earth movement and erosion, which have played a part in producing the final (often rather battered) whole. It is part of a logical attempt to get to the heart of the oil affair, to realise that oil finding is not a mere affair of dip hunting, but an application of all that we know of oil origin and migration to the particular geological history of the area we are studying. Yet these very achievements of geological thought are only made possible by detailed palæontological and stratigraphical researches.

One other important modern tendency—and one which it is a great pleasure to note—is the greater development of research—often in directions which are not of obvious economic value. Recently the American Association of Petroleum Geologists has resolved to form a committee to foster scientific research into aspects of the subject of a pure rather than an applied value. The welcome significance of this step is the evidence it shows of a band of enthusiastic workers eager to know the truth apart from its economic value.

Turning now to the various aspects of petroleum geology and confining attention to what has been done in the last two years, it may be logical to commence with the question of the origin of petroleum. The journal of the Institution has been enriched by the important paper of Taylor, giving a *résumé* of his discoveries in Egypt and Cambridge on the importance of base exchange in the

retention of a non-toxic environment for bacterial decay. His contention is that this result is achieved by the dilution of saline waters by incursion of fresh water. It is possible that his complete theory of oil origin will require drastic revision before it is acceptable, but his discoveries certainly throw new light on a difficult subject. Ideas die hard, one would have thought that the inorganic theory of the origin of commercial oil supplies had been decently interred, yet we still find the occasional protagonist for this, or rather one of these innumerable inorganic theories[1]. Of more interest is the discussion of the origin of Japanese Petroleum by K. Koyabashi[2] and his suggestion of the importance of the presence of acid clay in the last stages of the transformation of the organic material. Stahl comes to the conclusion that oils originate from black sapropelic muds in marine waters with the aid of iron or sulphur as catalysts[3]. It is of interest to note that recent American researches on the effect of heat and pressure on oil-shales and marine muds have not brought any fresh evidence to light.

Turning to the subject of oil migration we have the experimental work of Beckstrom R. C. and Van Tuyl F. M.[4] from which they conclude that compaction is the most important cause of oil migration. The general environment in which oil sediments are produced has received ample consideration in various regional treatises. A paper, however, of a more general type, dealing with the types of sand lenses in which oil is found is that of C. Brewer on the "Genetic relationship of oil reservoirs to shore line deposits"[5]

Among papers of structural interest, the still puzzling phenomena of salt domes receives further treatment by D. C. Barton[6], while we have an interesting discussion of American, German and Rumanian salt domes by O. Stutzer[7], who concludes that the oil relationship to salt domes is structural rather than genetic. M. V. Howard[8] gives a classification of limestone reservoirs which serves to emphasize the importance of interformational weathering to produce solution cavities for oil storage.

Of more general interest is the book on Earth Flexures, by H. G. Busk. It is written by one with an eye for topography, and a flair for ingenious synthesis, yet sometimes one feels that with so

[1] Le Bel. S. A. "Sur l'origine du petrole." *Bull. Soc. Chim.*, 1928, (4), 43; (6), 654–657.
[2] *Chem. News*, 1928, **137**, 46–47.
[3] Stahl, A. F. von, and Uusikirkko W. L. Montan. Rundschau, 1928, **20**. 18), 550–1.
[4] *Bull. Amer. Assoc. Petr. Geol.*, 1928, **12**, (11), 1049–55.
[5] *Bull. Amer. Assoc. Petr. Geol.*, 1928, **12**, (6), 597–615.
[6] *Bull. Texas Univ.*, 1928, **2801**, 7–59.
[7] *Z. prakt. Geol.*, 1928, **36**, (10), 178–181.
[8] *Bull. Amer. Assoc. Petr. Geol.*, 1928, **12**, (12), 1153–1161.

many unknown conditions of rock competency it is not wise to follow literally a purely geometrical solution.

As students of tectonics we welcome the treatises on regional earth structures, and there are at least two which deserve a more complete discussion than is possible here. Staub's monumental work[9] on earth tectonics and the translation of F. Heritsch's Alpine studies by P. G. H. Boswell.[10]

That such subjects as the fundamental causes of earth movements are of great interest to Petroleum geologists is indicated by the publication of the Symposium on the Theory of Continental Drift by the American Association of Petroleum Geologists. Finally, by the same institution we have the valuable publication in two volumes on the Structures of Typical American Oil Fields.

While dealing with the subject of structure one is strongly tempted to touch on the geological aspect of Geophysics. This subject, however, needs separate treatment. Suffice it for me to say that oil geologists have welcomed these new methods of attack with open arms. Physical methods of research into earth texture, the ability to feel downwards in terms of structural units and to peer, however dimly, through mantles of alluvium are all of immense value to the worker whose main interest is always beneath the surface. But it must be emphasized, the recent rapid strides in applied Geophysics are the result of collaboration of the geologist and physicist. The interpretation of results must always be in terms of geology, and the torsion balance, seismograph, etc., are but new weapons for geological investigation. It is of interest to record the excellent work done by H.M. Geological Survey in the investigation of the use of geophysical methods to elucidate geological problems. A record of some of this work is contained in the Institution's Journal[11].

In the realm of palæontology it would be invidious to single out individual papers from the mass of detailed studies that have been published. One publication of great general usefulness needs a passing reference, the work of J. A. Cushman, on the Foraminifera.

Studies of Areal Geology have been both numerous and of great interest. In the Institution's Journal, L. D. Stamp has given two papers, one on the oilfields of Burma,[12] and the other a more general discussion of the relations of oilfields to geosynclines.[13] Both these contributions are interesting examples of the attempt to explain oilpools in terms of environment as well as structure.

[9] Der Bewegungsmechanismus der Erde R. Staub

[10] The Nappe Theory in the Alps.—Fr. Heritsch, 1929.

[11] W. F. P. McLintock and J. Phemister. Geophysical Work in Great Britain. *J. Inst. Petr. Techn.*, 1929, **15**, 563–568.

[12] *J. Inst. Petr. Techn.*, 1929, **15**, 300–345.

[13] *J. Inst. Petr. Techn.*, 1928, **14**, 28–63.

Noteworthy among the publications on areal geology in the European Oilfields is K. Tolwinski's summary of the oil and gas fields of the Carpathians[14], the book on the geology of the Rumanian Oilfields by Karl Krejci Graf[15] and W. Kauerhowen's account of the German oilfields[16].

In the Institution's journal A. Wade has written an account of the position at Hardstoft, and concludes that under present conditions further search for oil is not an attractive proposition.

It is obviously unnecessary to deal fully with papers on North American areal geology. These get full treatment elsewhere, and are so numerous that discussion here is impossible. Some of these papers have, however, a broader interest by virtue of the subjects they treat, or the method of attack. Of maps published recently, that of the Oklahoma oil and gas fields will be found useful.[17] B. L. Clark's[18] paper on the Tectonics of the Valle Grande of California deals with an area of great importance. Of interest in Mid-Continent geology is M. G. Cheney's account of the History of Carboniferous Sediments of the Mid-Continent Oilfields[19]

In Canada, among other papers, that of G. S. Hume, on the Oil and Gas in Western Canada[20] gives a useful summary of information. The same author has contributed a paper to the Institution on a similar subject.[21]

As contributions to South American geology we have Steinmann's book on Peru[22], Stutzer's compilations on Colombia[23], and Liddle's account of the Geology of Venezuela and Trinidad[24].

My last comments on petroleum geology deal with that section where the geologist and engineer meet. Probably in no other branch of the science has the advance been so rapid in recent years as in petroleum production. This is now a subject in itself, and cannot be fully treated here, but all geologists interested in production methods will be keenly interested in the advances made in the process of repressuring the oil zones. One other question where the geologist and engineer meet is in the problem of the crooked hole. While the industry was mainly concerned with cable tool drilling, or even while the rotary wells were relatively shallow this was not

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[14] *Poland Geol. Survey, Bull.* 16, 1928.
[15] Die Rumanischen Erdöllagerstätten. Karl Krejci Graf.
[16] *Bull. Amer. Assoc. Petr. Geol.*, 1928, **12**, (5), 463–499.
[17] Oklahoma Geol. Survey publication.
[18] *Bull. Amer. Assoc. Petr. Geol.*, 1929, **13**, (3), 199.
[19] *Bull. Amer. Assoc. Petr. Geol.*, 1929, **13**, (6), 557–595.
[20] *Can. Geol. Surv. Econ. Geol. ser. No. 5*, 1928.
[21] *J. Inst. Petr. Techn.*, 1928, **14**, 669–676.
[22] Geologie von Peru. G. Steinmann.
[23] Zur Geologie und Mineralogie von Kolombien. O. Stutzer.
[24] The Geology of Venezuela and Trinidad. R. A. Liddle.

a very material point, but now that rotary wells extend to 8000 feet or more, the deviations from the vertical become very marked. The well spacing below ground becomes vitiated, the real depth of the well is not that which is logged, and geological data may be very misleading. The importance of this subject is now beginning to be recognised, and the question of drilling straighter holes, or alternatively of surveying the crooked holes is being tackled seriously. A recent contribution on this subject by F. H. Lahee[25] is well worthy of close attention.

[25] *Bull. Amer. Assoc. Petr. Geol.*, 1929, **13**, (9), 1095.

Geophysics.*

By W. H. Fordham, M.A., F.G.S. (Member).

General.

Ambronn[1] gives a valuable historical sketch of the development of applied geophysics and shows how closely the different methods are related to the corresponding branches of pure geophysics, which have been studied, more particularly, in observatories. As a guide to present-day geophysics the book is disappointing, for it was originally published in German in 1926, and only a part was brought up to date before it was translated in 1928.

Fordham[2] gives a summary of the geophysical methods used in oil geology, with results reported by various writers. The cost of instruments and surveys is included.

Heiland[3] is responsible for a full and graphic description of the manner in which geophysics are being developed and applied in the United States. Much of the material, of which he makes use, is derived from the special articles referred to later in this report.

The same author describes the work now going on in Germany.[4] Geological Survey Departments are carrying out experimental surveys on a large scale, in co-operation with instrument makers and exploration companies, with the object of improving instruments and methods for use abroad. The instruments made by the different manufacturers are described, and the activities of the exploration companies, the greater part of whose work is carried on outside Germany, are detailed.

Eve and Keys[5] give much valuable first-hand information on electric methods, but rely to a large extent on the reports of others for their descriptions of the remaining methods. They anticipate that the resistance method, of which they have made a close study, will become of importance in oil finding.

Gravity.

Instruments.—Shaw and Lancaster-Jones[6] give a full description of the gradiometer, an instrument designed to measure the gradients of gravity only. A comparatively small compact balance has been produced, with which observations can be made by day, and stations completed in less than two and a-half hours. This is the only authenticated instrumental improvement of the last two years.

* Paper received December 31, 1929.

Theory.—Very considerable advances in the treatment of terrain and topographical corrections, and in interpretation, have been described by Lancaster-Jones[7], Barton[8], [11], Heiland[9] and Shaw.[10]. The titles of the papers are an indication of their contents.

Practical Applications and Results.—Barton[12] points put that the torsion balance can only be used to determine geologic structure in cases in which irregular distribution of mass is concordant with the structure, and that relatively complete concordance is found in the case of salt domes, volcanic plugs, laccoliths and dikes intruded into homogeneous country rock. Partial concordance prevails in anticlinal, domed and fault structures.

Barton[12] states that three definitely and possibly five salt domes were discovered by the torsion balance in the Gulf Coast area in 1924-26, that faults in a number of districts can be indicated, and that in the Mid-Continent the buried ridges of heavy rock can be located.

McLintock and Phemister[13] give details of surveys of hidden structures carried out by the Geological Survey of Great Britain, and consider that the balance can be of great help in mapping concealed heavy rock masses and subdrift topography.

Belluigi[14] gives a summary of the geophysical investigations which have been carried out by the A.G.I.P. in the valley of the River Po, in Northern Italy, where geology alone is of little value. Four thousand gravimetric observations and several thousand electric tests have been made, and seven anticlinal structures located. Drilling has not yet taken place to test if these structures are oil bearing.

Seismic.

Instruments.—Heiland[15], Barton[16] and Ambronn[17] explain the principle of seismic instruments. Barton's account is the clearest and most concise. He states that the seismic method for mapping structures depends chiefly on the velocity of artificially produced earth-waves. To measure velocities it is necessary to observe the time of arrival of the waves, the time of the explosion causing the waves, and also know the distance from the shot point to the observation point.

Two types of seismograph are in use—photographically recording mechanical seismographs, and photographically recording inductive electric seismographs. The latter are known as geophones.

A seismograph consists of a suspended heavy mass, which tends to remain at rest when its supports move, a device to magnify the relative movement of the heavy mass and its supports, and a device to record these magnified movements.

The Mintrop mechanical seismograph, described by Fordham[2] and Barton[16], registers the vertical component only, while the Schweydar instrument, described by Heiland[15], measures both the vertical and horizontal components. Barton explains that these seismographs are more affected by surface tremors and wind than the geophones, for the mechanical instruments rest on the surface, while geophones are placed at the bottom of small holes.

The electric seismograph, or geophone, consists of a heavy mass, to which a coil of wire is fixed, supported on a spring. A permanent magnet with small air gap, in which the coil hangs, is fixed to the supports. The oscillations of the supports thus produce a fluctuating electric current in the coil. This current is amplified by means of a radio amplifier and recorded by a photographically recording galvanometer.

With both types of instrument the time of the explosion is recorded by wireless, light portable sending and receiving sets being used.

The distance from the shot point to the seismograph is frequently calculated from the time the air wave, due to the explosion, takes to reach the instrument. In the mechanical type the arrival of the air wave is usually registered, while with geophones special air wave receivers are used.

Types of seismograph are described by Ambronn[1], [17] and Rieber,[18] in which an electric signal, carried by an insulated wire, is used for recording the time of the explosion.

Theory.—Barton[16] explains that if a formation with a higher speed of transmission of the earth waves underlies one with a lower speed of transmission certain facts about the lower bed can be determined from the travel time of the waves. The speed of transmission is more or less proportional to the denseness and compactness of the formation. Unconsolidated sands, shales and marls transmit the waves with a low velocity, weak sandstones and limestones with a slightly higher speed and massive crystalline rocks (limestones, rock salt, schists, gneisses and plutonic rocks) with a very much higher speed. The use of the seismic method depends on the fact that earth waves travelling through rock of relatively low speed of transmission and impinging on the upper surface of an underlying formation with a higher speed are, in part, reflected back to the surface of the ground and, in part, refracted along the upper surface of the lower formation, and then refracted back to the surface of the ground.

If a higher speed bed underlies the surface bed at such a depth, compared to the distance between the shot point and observation point, as to be detectable, the seismogram shows the arrival

of a wave in advance of the direct or surface wave. The indirect waves are found for practical purposes to obey the optical laws of refraction. In many cases a high speed mass may act as a diverting lens, and a blind spot may be found to exist where the amplitude of the waves refracted back to the surface is greatly reduced. This so-called "absorption" is not uncommon in the Texas Louisiana Gulf Coast.

Barton and the other authors mentioned give formulæ applicable to different forms of structure.

Practical Applications and Results.—Barton[16] gives details of the constitution of a seismic troop and the way in which work in the Gulf Coast is carried out. In prospecting for new salt domes the receiving units, which may number six or more, are placed more or less radially along roads from four to eight miles from the firing point. If a salt dome lies within the fan one or more shots may show a higher speed than normal and may show the "absorption." To definitely establish a dome profiles are shot across the dome at different angles.

In mapping structures not of the salt dome type the method of reconnaissance by fan shooting is not possible. Most structures which the oil geologist wishes to map have a structural relief of only a few hundred feet, and to map them it is necessary to run profiles and map the surface of a relatively high speed bed.

Rieber[18] describes field operations in California where structures not easily identified are being investigated.

Barton[16] reports that the success of the seismic method in discovering new salt domes in Texas and Louisiana continues to be most brilliant. He gives a list of fifty-five domes and structures discovered by this method up to the middle of 1928.

Heiland[3], whose account was written a few months later, gives a somewhat longer list.

Bowman and Vetter[20] state that in the year 1928-29 twelve new domes or structures, discovered by geophysical prospecting, were reported in Texas and twenty-two in Louisiana. They continue that there apparently was a tendency among operators to favour the seismograph in prospecting for shallow domes, and the torsion balance for deep-seated domes and for outlining the shallow domes.

Rankine[19] describes an experimental survey carried out in Persia over a known oil-bearing anticline. He considers that the results obtained show that the method will prove of value in discovering other similar structures.

Hopkins and Wasson[21] state that gravitational, magnetic and seismic methods are being widely used in Venezuela, and that fields are being discovered where no surface structures are visible.

They conclude: "Sufficient time has not elapsed to measure the full value of the scientific methods brought to bear on the general exploration problem, and so much of the information is confidential that perhaps nothing of specific interest will ever get much publicity. However, as more and more wells are located in that flat country, far from seepages and evidence of surface structure the results obtained will soon lead at least to some very interesting inferences . . ."

Magnetic.

Instruments.—Heiland[23] gives a complete description of the Askania Field Balances, with underlying theory. They are knife-edge instruments. He states that, as a result of repeated practical tests, he is satisfied that under average working conditions station values accurate to within 5 gamma are obtainable. He considers such accuracy sufficient for the most precise geological work and that it is hardly probable that anything will be gained by merely increasing the sensitivity of magnetometers. Pautsch[26], Rieber[24], Barton[11] and Fordham[25], however, are of opinion that instruments more reliable than the existing types are desirable. Rieber describes an electric apparatus for measuring the vertical force; Fordham describes a torsion wire horizontal instrument and a modification of the knife edge vertical force balance; Pautsch suggests that the most satisfactory way of making relative measurements of the magnetic force at neighbouring stations will be to use an electric apparatus with which the difference in force at the two stations can be directly measured. He states that he has designed the requisite instrument, and will describe it in due course. If this new instrument proves satisfactory field operations will be simplified and corrections for diurnal variations and changes of temperature eliminated.

Jung and Geoffroy[22] describe a manner in which a magnetic theodolite may be used as a horizontal magnetometer.

Dye[27] describes an electric apparatus, designed at the National Physical Laboratory, for measuring the vertical force.

Jolly[28] describes the F. E. Smith horizontal magnetometer. This is a new electrical device used by the Magnetic Survey for measuring the horizontal force in absolute units.

The two last instruments are accurate to within one or two gamma, and are intended as magnetic survey instruments rather than geophysical instruments. It would, however, be possible to adapt them to geophysical purposes.

Theory.—Heiland[23] explains that there is a close relation between magnetic anomalies and oil deposits for the following reasons: (1) Oil fields generally lie in zones of relative uplift; (2) this uplift

is either produced by the deposition of the oil-bearing strata on pre-existing ridges of igneous material or by later processes of folding which elevated igneous material, or both ; (3) the igneous rocks thus associated with the oil-bearing formations carry magnetite which produces magnetic anomalies.

Heiland wrote in 1928 that two hundred instruments were in use in the United States, the operators in many cases not being capable of handling these delicate instruments, and few of them able to interpret the results. He continues : " Many an operator believes that all he has to do to find the oil is to look for a magnetic high on a small portion of land. Few realise that successful interpretation of magnetometer surveys cannot be made without a thorough theoretical understanding of the magnetic effect of certain types of magnetic bodies (that is, how it depends on latitude, orientation, dimensions, mineral content and geologic history of the stratum) ; also, that a small magnetic survey should, if possible, be evaluated only in the light of the magnetic character of the whole area and by comparison with other magnetic anomalies. The reason for this is that magnetic anomalies are closely associated with the geologic history of the deposit, because they depend on so many physical properties of the rocks (magnetic content, mechanical microstructure, previous temperature and pressure conditions, secondary or primary location, etc.).

" The properties just referred to are more numerous than those affecting the interpretation of other geophysical results, so that magnetic anomalies are much more difficult to interpret than torsion balance or seismograph results."

Spraragen[29] discusses the magnetic anomalies accompanying oil structures and points out that both magnetic highs and lows may indicate places suitable for test drilling.

Practical Applications and Results.—Barton[15] reports that he had to do with extensive tests of salt domes in the early days of magnetic surveying, but that although the presence of the domes was indicated, the indications were far less reliable than those given by the torsion balance or seismic methods. The instrument, however, had considerable power in mapping certain granite ridges.

Spraragen [29] gives details of field operations, together with the results of a number of surveys over known oil-bearing structures. From these surveys he concludes that magnetic surveying will prove of very considerable value in oil geology in locating similar structures.

Jung and Geoffroy[22] show that faults in Lorraine can be located magnetically and discuss the application of their results to the search for oil in the plains of that country.

Hallimond[30] describes a series of observations carried out by the Geological Survey over the Swynnerton Dyke in Staffordshire. These measurements show that the course of the dyke can be mapped magnetically, and the inference is that other similar structures can be located by the same method.

Barret[31] states that serious magnetic surveying started about four years ago in the States, that three hundred instruments are now in use, and that the number is increasing. He reports that the results obtained are varied, some being gratifying, others disappointing. The failures he puts down, in many cases, to errors in field observations. Details are given of precautions to be taken while surveying.

Electric.

Inductive Method.—Sundberg[32] describes the theory underlying the Swedish large rectangular horizontal loop inductive method of finding the depth of a conducting horizon. If a conducting bed underlies the loop a secondary field is produced, which is out of phase with the primary field, and by studying the phase relations and intensities of the two fields the conductivity and depth of the conducting layer can be estimated. Depth figures can be obtained on an average at ten points each day, and observations at two or three points per square kilometer are sufficient for reconnaissance purposes. The method is useful when oil is associated with salt water, for by finding the upper limits of the salt water it may be possible to locate the oil.

Sundberg states that surveys have been carried out for the Vacuum Oil Company for some years.

Resistance Methods.—Eve and Keys[5] describe a complete investigation carried out by them of four resistance methods: (*a*) the porous pot method, (*b*) the Gish-Rooney method[34], (*c*) the "megger" method[33] and (*d*) the single electrode probe method. They consider that these methods can be used to find out whether a relatively good or bad conducting layer exists below any given spot. They point out that one of these methods (*d*) has been used with success by Schlumberger in Alsace for locating salt domes[35], [36], and suggest that this, or other resistance methods, may prove of great value in oil geology.

The principle of resistance methods is to use four earth electrodes, connecting a current generator to the two outer electrodes and then measuring the current between the outer electrodes and the E.M.F. between the inner ones. If a direct current is used in the current circuit, non-polarising porous pot electrodes must be used in the potential circuit. If an alternating or interrupting current is used all the earth electrodes may consist of metal spikes.

The electrodes are spaced in such a manner that approximate formulæ can be calculated for the earth resistance between the potential electrodes. In the porous pot, Gish-Rooney and megger methods the electrodes are placed in a straight line at equal intervals apart, Wenner's formula being applied :—

$$p = 2\pi A \frac{E}{I}$$

where p is the average resistance of the formations between the potential electrodes to a depth of about A,

A is the distance between the electrodes,

E is the E.M.F. between the potential electrodes in millivolts,

and I is the current in the current circuit in milliamperes.

In the single electrode probe method the current electrodes are placed far apart, and measurements made with the potential circuit on a radial line through one of the electrodes.

In this case the formula used is :—

$$p = 2\pi \frac{ab}{a-b} \frac{E}{I}$$

where a and b are the distances of the potential electrodes from the current electrode at which it is desired to "probe," E and I have the same meanings as in the previous formula, and p is the average resistance of the formations below the "probe" electrode to a depth of approximately b. This formula is only true provided b is less than one quarter of the distance between the current electrodes : that is, if it is desired to test the conductivity at a given point to a depth of 1 000 ft., the distance between the current electrodes must be about 5,000 ft.

By taking a series of measurements with different values of A in the first case, and a and b in the second, the changes in conductivity with depth can be found. They are most clearly seen by plotting p against A in the first case, and against $a + \frac{b}{2}$ in the second, a change in conductivity manifesting itself by a break in the curve.

Eve and Keys give full details of apparatus and method of carrying out field surveys.

For the metal earth electrodes they use pointed pieces of $1\frac{1}{2}$ in. $\times$ $1\frac{1}{2}$ in. $\times \frac{1}{16}$ in. galvanised angle iron, 16 in. long. They describe a simple manner in which non-polarising electrodes may be made from Daniell cell porous pots. The current leads are insulated wire in lengths of 500 ft., each length being on a separate reel. These lengths are linked together with well-insulated connectors. In the porous pot and single electrode probe methods high tension radio

dry batteries may be used as the source of current. These are joined in series to produce an E.M.F. of from 50 to 150 volts. In the current circuit the measuring instrument is a milliammeter, and in the potential circuit a slide wire potentiometer, reading to one millivolt. The milliammeter should have four ranges, 0 to 5, 0 to 50, 0 to 200 and 0 to 500 milliamperes; while the potentiometer should have ranges 0 to 100 and 0 to 1000 millivolts.

The Gish-Rooney apparatus uses similar batteries and measuring instruments. Its distinctive feature is a double commutator which reverses the current in the earth circuit about thirty times a second, while causing interrupted currents to pass through the measuring instruments.

The "megger," made by Evershed and Vignoles, is a compact direct reading instrument which measures the $\frac{E}{I}$ ratio by means of an ohmmeter. Its primary use is for testing the resistance of lightning conductor and other "earths," and its application to geophysics is due to Lee.[33] The instrument consists of a hand-driven direct current generator, with a current reverser and potential commutator on the same shaft as the generator, together with an ohmmeter. The current in the earth circuit is rapidly reversed; while the currents passing through the two coils of the ohmmeter are direct currents.

Eve and Keys point out that the "megger," or possibly some other design of alternating current apparatus, could be used in the single electrode probe method in place of the direct current arrangement described.

Radioactive Method.—Lee[37] is responsible for the translation of an account of a series of Russian investigations in which penetrating radiations were measured. One of the experimental surveys consisted of a traverse across an exhausted part of the Maikop Oil Field. The radiations are said to have been more intense above the oil sands than elsewhere.

The value of these observations is somewhat discounted by experimental work on the same lines mentioned by Eve and Keys[5], who report that one of them worked at the subject for more than a year with discouraging results.

The Growth of Geophysics in the United States.

Barton says that four torsion balances were imported into the States in the autumn of 1922. The first salt dome discovered with these instruments was the Nash dome, located early in 1924. Within two years of this date more than one hundred balances are said to have been in use.

The Seismic method was introduced late in 1923 and several salt domes were discovered about a year later. The number of seismic troops in the field in 1929 is given as 28.

The first magnetometer was imported in March, 1924. It was established in 1925 that certain granite ridges could be mapped by this instrument. By the end of 1926 60 magnetometers were in use, and the number has now increased to 300.

Cost of Surveying.

Barton gives the cost of running a single torsion balance as $1200 a month, during which time fifty stations should be done. With the gradiometer, mentioned earlier in this report, a very much larger number of stations could be completed per month.

Barton says that the cost of operating a standard seismic troop in the Gulf Coast salt dome area is reported to average between $15,000 and $20,000 a month.

Spraragen estimates that the salaries and running expenses of a three-instrument magnetic survey party amount to $1700 a month, 75 stations a day being done on the average, on five days each week. This estimate does not include depreciation of instruments or cars.

Edge [36] considers that three months' field work with an electrical unit, consisting of two operators and equipment, would probably involve a total expenditure of £2500 to £3000.

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Oilfield Practice.*

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Incessant improvements in plant and materials designed to accelerate drilling progress and reduce the number of delays and hindrances, due to defective material and human imperfections, have characterised oilfield operations in 1929. Each year deeper drilling leads to demands on manufacturers for improved machinery and higher quality of material, and no disinterested observer could deny that the engineer's response is commendable.

Wells were being regularly drilled to 8000 ft. in 1929 with no more difficulties than those of 5000 to 6000 ft. a year or two ago. In several fields, such as Santa Fe Springs, Kettleman Hills in California, Oklahoma City Pool, Oklahoma, and in parts of Texas, excess of this depth is becoming general. Much greater attention was paid to the verticality of wells as additional data came to hand showing to what extent deviations from the vertical have misled geologists and operators in their predictions. An analysis by Alexander Anderson of some 255 rotary drilled holes in California, involving a footage of 1,158,542 ft., showed that the average drift varied from 10·6 ft. at 500 ft. to 793 ft. at 6000 ft., declinations of as much as 65° being noted at depths of 6000 ft. He has very pertinently remarked that customary deflections represent a shortening of vertical depth, which entirely upsets correlations. This shortening averaged 115·6 ft. in wells between 5000 and 6000 ft. deep. The disposition of bores to deflect with increased depth where surface judgment by feel is less easy is indicative of diminished control over tendencies, and suggests the lines of attack for remedies. No rule has been found to account for the direction and amount of drift, although changes in the nature and dip of the strata are perhaps the dominating cause. It has been stated that where the dip of beds is below 10° the drill tends to deflect into the structure, and at greater dips the bit is inclined to follow down the dip. A wider recognition of the evils of deflection, and the general acceptance that it is to a large extent dependent upon the rate of feed, have driven more operators to adopt automatic feeds or to introduce means of registering the weight on the bit. The frequency of twist-offs in rotary drilling is probably largely due to misjudging the weight on the bit as different kinds of strata are encountered.

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Two automatic feed controls of American design still hold the field —namely, the Hild and the Halliburton; and both depend upon torque for their action, and have been widely used. The former is only applicable when electric power is available, so that its superior claims are neutralised by this disadvantage where electric power is not supplied. The great expense of the automatic control devices has led many operators to confine themselves to the use of weight indicators which give the driller an approximate figure upon which to adjust the feed to the bit. Self-registering weight indicators of fair accuracy can now be purchased, and intelligent use of the information imparted in this way not only saves much drilling trouble but gives useful data to the geologist.

No general rule so far appears to have been established for fixing approximately the most useful weight for various rocks at different speeds. Recorded safe pressures on fish-tail and rock bits appear to vary between 6000 and 20,000 lbs.

Apart from general improvements in quality and heat treatment of steel in drill-pipe, the usefulness of rubbing discs (protectors or stabilisers) appears to have been the chief innovation. Until these were put into use the vibration and friction between the drill-pipe and well sides was not perhaps generally realised, but employment of rubber discs in modern rigs is now general. The use of these rubber protectors is not confined to that part of the drill-pipe working in casing, but they are attached near the bit, and it is claimed, without the accidents one might be inclined to anticipate.

Flush-jointed heat-treated drill-pipe and flush-jointed tool joints have been introduced for use with rotary drilling machines having hydraulic feed and pressure control. The flush-jointed drill-pipe is to allow its passage through a stuffing-box which holds the pressure.

Mud pumps are being constantly improved to deal with heavy mud fluids at higher pressures (usually 1000 lbs. per sq. in.). A stroke of 18 ins. has been reached in some designs, but contrary opinions are held regarding the best length of stroke and, indeed, concerning the velocity of mud fluid in the hole. It is claimed that excessive velocities tend to destroy the mud lining of holes and encourage disintegration of the walls of the bores. The main aim seems to secure a thorough flush close to the working face of the bit to remove cuttings quickly and to keep down temperature.

A spirited controversy still ranges around the weight and nature of muds for circulation. Some claim that thick mud has a very serious disadvantage in hindering progress and tending to plaster up the walls to a dangerous degree, and they claim far higher drilling speeds with thin muds. The virtues of mud and heavy

colloidal fluids can certainly be unnecessarily magnified, and its natural use should be dictated by a number of factors relating to the nature of the strata, the type of bit used, and the gas pressures encountered. When the drill-pipe cannot be raised through over-plastering the walls with mud, circulation with oil and water or oil alone has proved effective.

Very promising experiments it is said have been made with reverse mud flush on the Gulf Coast fields of U.S.A. The very obvious advantages of relatively low descent velocity and high velocity ascent where it is needed to raise the cuttings are, to some extent, offset by the more elaborate surface arrangements necessitated; nevertheless, it is claimed by some that important developments may be expected in this direction during the next few years.

The great size and weight of modern high-pressure reciprocating mud pumps is leading manufacturers to consider the construction of turbine pumps. Present type mud pumps have a working displacement efficiency of 60 to 70 per cent. in practice.

The recognised need for higher rotary speeds to accelerate cutting, and the acknowledged limitations to about 150 revolutions minute when long strings of drill-pipe are used, is causing engineers to give serious consideration to the construction of a mechanism which will cause the rotation of the bit only. The idea is not novel, but such difficult problems are involved that much time and money will have to be spent on experiments before a workable mechanism is produced.

Attention is being given to the construction of full-size portable rotary rigs designed to permit quick transfer and assembly. Some of the designs seen have various major parts separately mounted on frames which can be quickly coupled on arrival at site.

A form of spiral drill-stem has been introduced for attachment above the bit. A stem of this design can be kept to about the same size as the drilling bit, so that there is little disposition to deflect from a vertical direction. The flushing fluid is carried in a pipe along one of the flutes. To the writers' knowledge the use of spiral stems in percussion drilling has proved of great help in preventing deflected holes where hard and steeply inclined rocks had to be pierced.

Greater use is being made of special alloys for facing fish-tail bits, and every year better footage is being made before dressing is necessary. Many alloys are now on the market, and further discoveries may be safely anticipated, for it is recognised that as drilling gets deeper the need for reducing the number of withdrawals becomes increasingly urgent. Rock bits are being constantly improved to deal with hard strata which a fish-tail or disc

bit will not face, but there are still cases where it pays to use percussion tools for piercing a mass of hard rock which wears the roller discs flat in a very short time.

When steam is used for drilling much better and larger boilers are being introduced than formerly. Considerable attention is now paid to fuel consumption on oilfields, and it is usual to instal multitubular boilers with 350 lbs. working pressure. Field boilers of 5000 lbs. per hour evaporation are on the market. Naturally good water must be made available for such boilers, and this often means the addition of water-softening plants. One writer has stated that in West Texas some boilers do not outlast the drilling of a single well—due, presumably, to the use of badly mineralised and corrosive waters which have not been treated.

The introduction of a syphon leg from the throat plate to the crown sheet of the boiler firebox has met with success. Besides a big saving in fuel, it is claimed that incrustations are lessened and that it affords protection to the crown sheet in the event of lowness of water in the boiler.

Coring devices have been so rapidly improved that coring is a general practice almost anywhere now once interesting horizons are being penetrated.

The design of efficient core barrels has attracted an unusual amount of attention during the last year on account of the necessity of examining samples taken from great depths under a pressure of mud fluid which often masks their true character. Various arrangements are often improved to extract *samples* of strata, but there is now a general demand for appliances which extract a real core showing features lost in a mere sample. There are now many core barrels on the market which will take and preserve cores many feet in length. Once interesting ground is reached in deep territory it is usual to core the whole distance till the well is finished.

A record of the deepest well in Texas in the Big Lake Pool, Regan county, has been published, and illustrates forcibly the advance in drilling technique. The well was drilled to 8343 ft. in 875 working days, of which 394 were drilling days. The total cost was $141.500, or $16.60 per feet, of which $51.040 or $6 ft. represented labour. Within fourteen months the well gave 100,000 bls. of 60° Bé (0·736) oil with a gas-oil ratio of about 10,000, the gas containing 1·8 gallons of gasoline per 1000 cub. ft. The temperature recorded at base of well was 170° F. At 6500 ft. it was 135° F.

Last year witnessed a serious oil well fire at Moreni, Rumania, where for many months it has defied all efforts to extinguish or control. It was one of the deep wells carried to the Meotic beds on the south of the salt and near the junction where gas had concentrated. On striking the source the drill-pipe was violently

expelled from the hole and the gas took fire, and since then an apparently undiminished pressure has been sustained, and a column of flame rises some hundreds of feet in the air, a prey to the winds. Efforts to cap the well with shields failed, and tunnels driven towards the well proved of no avail, as gas impregnated the loose and fractured sediments, causing explosions and accidents which forced their suspension. Neither International Authorities nor local talent has so far been able to advise a course which gives reasonable grounds for anticipating success. Appearances encourage the belief that the eruption is mainly gas, but the escape of tens of millions of cubic feet daily from a structure where the maintenance of pressure is a factor of the greatest importance in helping the movement of viscous paraffinous oils is a source of serious local concern.

The above event serves to emphasise the necessity of extreme caution when drilling into deep-seated oil-bearing strata where pressures of several thousand pounds per square inch are to be anticipated. Owing to the great caution exercised when drilling deep fields, there have been remarkably few cases of cratering and big fires in oilfields lately, although much deep and dangerous work has been successfully carried out.

A number of improved fittings for the control of high pressures and the regulation of flow have been introduced, some of the make-ups for casing heads wherein the space between successive columns of casing is sealed, representing very fine workmanship. A more or less standardised form of Christmas-tree fitting has been evolved in California for the control of the deep, high-pressure wells, and this pattern has been adopted elsewhere with success. The surface flow arrangements are tied to the casing by heavy bolts, and a combination of valves and fittings enables the flow to be checked or deflected into smaller or other beans if one is too large or becomes worn and needs a new liner. By a careful adjustment of size of bean a flow can usually be adjusted to give an acceptable gas-oil ratio, and also a sand percentage where the beds are of the uncompacted variety.

In Russia, Rumania, and Venezuela, where the sand conditions are often bad, wells are now being brought into production under pressure without excessive sand or oil-gas ratios.

The attachment of flow nipples at the bottom of the tubing instead of the top has many times been proposed and has been tested in Texas, Wyoming, Venezuela, California and Oklahoma, mostly with inconclusive results. Although on theoretical grounds the bottom bean would appear advantageous, there are so many difficulties in adjustment and replacement, besides being exposed to invisible influences, that its use is rarely attempted.

Emulsion problems still exercise the ingenuity of engineers in some fields when the flow pressure falls. Flow nozzles (beans) are particularly apt to cause emulsions when the appropriate conditions are present, and the best plan is to promote a separation of the oil and water under pressure in a vessel before the nozzle is reached. Tretolite has proved quite useful in many cases, but it has been found advisable to apply the chemical to the oil after the nozzle and not before, or emulsions may still appear.

Air-gas lift has continued to yield good results in the newer fields of America, and its use has spread to fields in other parts of the world. Very satisfactory results have been obtained in Rumania, where one large property was operated solely on gas-lift for a time. The reduction of gas pressure and consequent fall of fluid level in some of the leading American oilfields has led to some modifications in methods to meet the new conditions. Intermittent gas-lift is now largely practised where the small ratio of submergence necessitates a heavy input of gas or air to maintain a flow of oil in the nature of a spray. By intermittent admission the air-gas consumption has been greatly reduced and the gasoline content of the oil improved, and sometimes the yield of oil has been raised in addition.

Various mechanical contrivances have been designed to effect admission of air-gas at prescribed intervals ; a water balance being the most general. There are obviously innumerable ways by which intermittent injection of air could be automatically timed. Each well needs separate adjustment to suit its peculiarities, and this adjustment can only be found by trial.

Attention has been called by one writer to the value of introducing a pinhole some distance above the working fluid level, thereby reducing the starting pressure considerably.

Some difficulty has been found in determining the stage when air-gas lift should be replaced by pumping in those fields where the static level of fluid has fallen considerably, especially where the wells are deep and pumping involves rod trouble and perhaps sand difficulties. Some close observers have maintained that it usually pays to install gas-lift at an early stage in natural flow period, as the gas-oil ratio can be substantially reduced with ultimate, if not immediate, advantage. In all cases it is agreed that no rule can be prescribed for fixing the depth of tubing and the input of air gas to give the largest yield or alternately the most economical gas-oil ratio. The use of tapered tubing has been largely discarded owing to the difficulty of determining a suitable combination to suit changeable conditions.

Attention has been directed by one writer to the injurious influence of placing the bean far from the well head, and the ill-effects of

relying upon the back pressure in the gas separator for control. He advises the use of needle valve flow beans. The need for avoiding gas pockets due to unnecessarily high points in a flow-line has been stressed by a writer, who states that in two cases an increased flow of 20 per cent. was obtained by flattening out such high points.

Much more success has attended the use of pumps in deep wells than was thought possible some few years ago. In both California and Oklahoma wells 4000 to 5000 ft. are being successfully and profitably pumped. In the Seminole field wells yielding as low as ten barrels a day of 38° to 41° Bé oil are being pumped when the conditions are favourable, and in California 25° to 35° Bé oil is being regularly pumped.

Engineers have shown by experiment that theoretical calculations are gravely upset by factors as variable as they are numerous, but a growing recognition of the principal causes for failure of pumping outfits is resulting in great improvements. Obviously crooked holes account for a mass of troubles to tubing and rods besides high-power consumption, but the accidents and expense caused by this frequent and irreparable condition can be reduced by attention to many details. Recent investigations in the California and the Mid-Continental Oilfields of U.S.A. have proved that pumping troubles can be greatly alleviated by :—

(*a*) Careful balancing of pump rods ;

(*b*) Adjusting speed of pumping to suit the well ;

(*c*) Providing effective gas anchors to insure the separation of gas before the oil reaches the pump ;

(*d*) Selecting a type and size of pump best adapted to local conditions.

Rod breakages have been greatly reduced by using heat-treated and special steels, and it is in this direction rather than in thickening-up the rods, involving extra weight, that improvements can be expected.

No general agreement has yet been reached as to the best way of balancing a mile of $\frac{3}{4}$-in. rods to avoid dangerous stresses at certain points. Some balance with weights on a beam, others with counter-poises on a band wheel or on a crank: but there is undoubtedly an opening for improvements in well-balanced surface gear. Speed adjustments are often rendered difficult by the use of electric or gas-engines drives which only allow of narrow fluctuations of speed, but it has frequently been proved that not only are rod breakages reduced by a slower rate of running, but as much or more oil is produced.

Measurements of volumetric efficiencies on deep wells in California and Oklahoma have shown the remarkable high percentage

of 30 to 60 per cent., with extremes of 2 and 105 per cent.; the percentage representing the ratio between the pump displacement measured by the stroke of the polished rod at the surface and the measured output of fluid.

Both rod and internal tubing wear is still a serious problem in some fields, and various guide or rubbing discs have been tried, but at Seminole difficulties were met with collar wear on the tubing due to abrasion occasioned by tubing movements during pumping. What at first sight seemed a simple matter to remedy proved much more difficult, as rubber or canvas wrappings bound at intervals to the tubing eventually suffered damage and led to their fragments entering the pump, or else the binding straps corroded, released the protectors and led to trouble.

An American engineer has shown that in Seminole more than 70 per cent. of stoppages were attributable to defects in sub-surface equipment, and some 16 per cent. to surface gear in a group of pumping wells under close observation.

Tests with dynamometers have shown that the call for such over-powered motors for pumping arises from the necessity of providing for brief demands far in excess of the normal in order to overcome inertia and take up unusual strains. As a matter of fact, 40 to 50-h.p. gas engines or electric motors have proved suitable for pumping 4000 ft. to 5000 ft. wells with $2\frac{1}{2}$ in. by 10 ft. working barrel and $\frac{3}{4}$-in. rods. At Seminole the indicated h.p. at a well tested fluctuated between 20·5 to 28·2 h.p. under varying speeds and balancing arrangements.

Repressuring of depleted oilfields has not made the advance expected on account of the continued low price of oil, but the time will come when much more will be undertaken. It is claimed that these methods give expectations of a 30 to 60 per cent. increased yield of oil. A certain school favours repressuring in the early stages of production when the oil is in the most favourable state for movement; but, on the other hand, high-pressure work in California has not apparently been attended with the results anticipated, and some experiments have been suspended. The expensive nature of high-pressure work discourages all but the largest concerns, and there is always the difficulty of arranging the co-operation necessary where unit operation is not in force.

Field and laboratory experiments are being continued to ascertain the actual relationship of oil and gas in the sands. A correct conception of original earth pressures, temperatures, and state of occurrence would materially assist those investigating production problems with a view to the conservation of oil.

The relative merits of air and gas as agents for repressuring is still debated. Obviously there are times when the necessary

volume of gas is not available except, perhaps, at considerable expense, and some difficulty. There are in addition other factors connected with use of air as a propulsion agent, such as the danger of compressing air-gas mixtures, and the corrosion of tubing and well fittings where air is used. Of academic, if not great practical importance, is the conversion of the oxygen of air into carbon dioxide and the changes effected in the quality of the oil. The exhaust gases of oil engines have sometimes been added to re-cycled air and gas mixtures to avoid the formation of explosive mixtures.

An arbitrary figure of 11,000 cu. ft. per barrel has been named as a reasonable ratio for repressuring, involving a cost up to 5 cents per 1000 cu. ft. of gas compressed in the Mid-Continental Oilfields of U.S.A. One experienced operator has stated that, contrary to usual statements, air is a better propellant than gas, and the objections to its use lie in the directions just mentioned.

Mining oil sands has made little progress, like other processes designed to recover the dregs of depleted or undeveloped oil sands where no gas remains to expel the oil. Work of a very elaborate character at Campina, Rumania, designed to mine the depleted oil sands of that once famous field has been suspended, due, it is said, to water difficulties; but, on the other hand, very interesting operations are just starting in the Bushtenari field, Rumania, where a shaft has reached oil sands which seep fresh light oil. The unexpected fact was brought to light that certain higher sands, formerly productive, proved practically dry on being reached, and the shaft had to be carried deeper than anticipated.

Persistent efforts are being made to recover the contents of the Alberta tar sands *in situ* without recourse to mining. Many devices have been tried to heat the sands to a temperature which would induce a flow of oil into wells. The problem is one of extreme difficulty, as the bitumen is a bad conductor of heat, and once the bitumen is rendered fluid the sands are unstable, as the grains are cemented together by the bitumen. As a road material these are likely to have a good value within the radius of cheap transport.

Unusually difficult drilling and production problems face those operating in the Turner Valley Oilfield of Alberta, Canada. No very satisfactory explanation has yet been evolved to account for the high concentration of light oils and gas at certain horizons in the Madison limestones. Very high pressures are met with, and the unrestricted release of gas, voluntary or involuntary, causes such a reduction of pressure that the moisture present freezes and the wells are obstructed with ice. If the wells get out of control before arrangements have been made for their regulation, or closing, the task of completion is a formidable one. Only special high-pressure fittings are used, and elaborate arrangements for

anchoring the casing and well heads must be made. The Kettleman Hills field of California presents some characteristics resembling that of the Turner Valley field, as the original well at 7000 ft. was estimated to be producing 4000 barrels of 60·5 Bé oil as a spray with some 36,000,000 cu. ft. of gas.

The gas-oil ratio controversy has advanced a stage during the last year by official attempts to enforce a minimum gas-oil ratio on operators in California and Rumania. Probably no responsible technologist doubts the value of gas conservation and the importance of controlling back pressures on flowing wells, but the subject of official control would appear to be linked up closely with that of offsetting and lease areas. The geological conditions are certainly very different in the two places just named, and in Rumania the peculiar structural conditions must naturally lead to very different production results at varying distances from the salt masses. One only has to turn to Alberta, Canada, to find an absurdity if gas-oil ratios as commonly understood were enforced. Here the gas-oil ratio may be 100,000 to 200,000 cu. ft. per barrel. Much the same sprays of gasoline characterised the early shallow development of the Surakhany oilfield of Baku, Russia.

The rational utilisation of gas can only be secured by the unit operation of oilfields which continues to excite general interest. Under these conditions wells could be located and spaced in an orderly plan designed to retain gas pressures in the domes and "highs," and wasteful wells could be closed in altogether.

Gas-gasoline extraction plants have been greatly extended where new rich fields have been developed. The annual production is now about 800,000,000 gallons a year in U.S.A. alone, and but for the low price of the product it would be much greater. The utilisation of surplus dry gas is still a serious problem on many fields remote from cities and fuel-consuming industries. The supply of oilfield gas from which the gasoline has been abstracted to the town of Ploesti in Rumania is an innovation of some importance, and the financial issue will be watched with considerable interest. General satisfaction has been expressed by those using the supply.

An experiment which will attract world-wide interest is that being undertaken by one of the chief operating oil companies in California, where surplus gas is being employed in a plant designed to extract nitrogen from the air. Chemists are incessantly engaged on seeking ways of turning to useful account the great volumes of gas burnt for disposal or allowed to dissipate in the atmosphere in some of the oilfields of the world.

Natural Gas.*

By S. C. Carney.

Natural gas service is available anywhere in the United States, though in many places it will be delivered as a liquid. Three-fourths of the gas sold in the United States is natural gas, and the total sales for 1928, as compiled by the American Gas Association, were :—

Natural	1600 billion cu. ft.
Manufactured	490 „ „

During a little more than the year 1929 natural gas has been delivered by pipe-line to San Francisco, Oakland, Salt Lake City, Denver, El Paso, New Orleans, Memphis, St. Louis, Birmingham, Atlanta and scores of smaller cities, in the greatest expansion programme ever known to the industry. Though a number of these cities were supplied late in the year, sales of 1,800 billion cu. ft. for 1929 are probable. Whereas a few years ago a gas trunk line 250 miles long was the limit that had been reached, at least three trunk lines 450 miles long, with 30,000 horse-power of compressors each, are now in operation, and one from West Texas to Chicago is contemplated of 900 miles length.

There are a number of reasons for this expansion. The older natural gas distributing companies have been successful financially. Their experience for the past twenty-five years has shown that gas reserves can be appraised by competent geologists and engineers, and the recent increase in value of their stocks has resulted in making capital available for new construction. Too much importance cannot be given to the useful effect of setting up, largely in the last ten years, of intelligent and compensatory rates. From its beginning, and for many years, the industry was seriously retarded and waste promoted by too low rates. It could not grow on flat rates of $2·00 per month per stove, or of 25 c. per month delivered in the city. It was the work of years by many people to accomplish the establishment of rates which, though still lower than other forms of fuel, are now causing the almost nation-wide availability of this ideal heating service ; if one consider propane, it is nation-wide.

Also the point of view of the oil-producing companies has changed. From considering gas as a rather troublesome incident in their business, better engineering methods have shown that gas

* Paper received November 27, 1929.

is of major importance in oil production. This has been officially recognised by the American Petroleum Institute. The broad subject, "The Function of Natural Gas in the Production of Oil," is treated at length in their publication under that title.

Whereas formerly a gas company could not lay a pipe-line into a new producing territory because the oil producers would blow all the gas away, and they blew the gas away because there was no line there to which it might be delivered, one now sees combinations of important oil companies jointly setting up their gas reserves for a line to St. Louis or Chicago.

But it is not as easy as all that. Waste of gas as reported by State officials in California alone—and California is the greatest gas-consuming State—is at the rate of 250 billion cu. ft. per year, which is five times the sales of an important company with 3,400 miles of lines and 113,000 consumers, or is in actual weight seven million tons of gas. It can be said, however, with certainty that the tendencies are now in the right direction. The California Gas Conservation Law, effective September 1, 1929, legalises combinations for the control of gas production, and requires the shutting-in of wells which produce, together with the oil, an undue gas volume which cannot be utilised. Since its provisions really express the enlightened self-interest of the best informed producers, it is confidently expected that waste will be greatly reduced.

Waste of gas is almost entirely confined to Oklahoma, Texas and California. These States have recently been provided with greatly enlarged distributing facilities, and it is encouraging to note that West Virginia, whose gas is most carefully conserved, has been delivering into industrial systems for over forty years, and yet produced two billion cu. ft. more in 1928 than in 1927.

Since much natural gas is sold locally, and at very low prices, only the crudest estimate can be given of its total sales value. This is probably not more than $400,000,000 annually for the entire U.S.A., as compared with more than two billion dollars for the sale of electric power. As against this gross income is an investment of approximately $1,750,000,000 in 57,000 miles of pipe-lines and accessories.

Average retail prices for domestic uses are 62 c. per M. cu. ft., and for industrial uses 16½ c. per M., and 1,000 cu. ft. of average natural gas contains one million B.Th.U. These rates are still very low, but the newer installations are starting with considerably higher ones.

Pipe-Line Construction.

Expansion in the industry is due not alone to better conception of gas values and quantities and to greater availability of capital,

but also to a remarkable advance in the technique of pipe-line construction. The outstanding item in this is a new electric-welded pipe. Since the first shipment of this in September, 1927, more than 2500 miles, in sizes from 10 to 22 ins. diameter, have been laid. One producing firm has now capacity of 26 miles per day of this pipe in diameters from 8§ to 26 ins. It is made from steels in the 0·20 to 0·30 per cent. carbon series with minimum tensile strength of 60,000 lbs./sq. in., considerably stronger than steels ordinarily used in pipe. The sections, usually 30 to 40 ft. in length, are formed cold from a sheet from which all millscale has been removed by pickling, and the longitudinal seam is then made by automatic electric welding. By use of these higher grade steels and less wall thickness, a 24-in. pipe of this type weighs only about 3 lb. more per foot than a 22-inch pipe of conventional manufacture, thus giving 20 per cent. greater capacity for 3 lb. per foot greater weight.

Corrosion.—Shop removal of scale and shop painting or wrapping affords great advantage in corrosion resisting, and, besides this, thoroughly practical machinery is available for hot coating and wrapping pipe either in shop or field with a spiral felt or paper composition impregnated with suitable asphalts, tars, or other corrosion-resisting materials at a cost much less than using a greater thickness of metal as a corrosion resistant. It is usually considered best practice to give pipe a preliminary shop coat and then to protect further in the field, as indicated by soil character.

Field Joints.—The rubber gasketed couplings are still in use, but electric and oxy-acetylene welding of field joints is rapidly displacing them. Pipe 40 ft. long instead of the former 20 ft. means half as many joints, and caterpillar type tractors equipped with winch and boom make the larger joints easy to handle. A bell and spigot type of welded joint offers many advantages in field construction, gives a smooth inner surface to the completed line, and places the weld in tension or compression but never in shear. To overcome the disadvantages of too great rigidity in an all-welded line, steel expansion joints, of the corrugated type formerly made only in copper, are available. A recent large line used 110 field electric welding units. These are gasoline-engine driven generators of 300 to 400 amperes capacity at 25 to 30 volts, each mounted on wheels so that it may be moved along the line as needed by a truck or tractor. Acetylene generators and oxygen cylinders are similarly mounted for gas welding. Automatic field-welding process has yet to be perfected, present methods requiring trained welders and methods being to a small extent trade secrets, with much discussion as to the best type of welding rod.

Construction.—The digging of trench and back filling are also largely mechanised. In hard rock, of course, some hand work is still necessary, but portable air compressors and air drills make the holes for explosive, reducing hand work to a minimum.

The pipe-line issue of the *Oil and Gas Journal* (August 29, 1929) carries advertising and descriptive matter pertaining to modern pipe-line machinery, and the most comprehensive map of gas pipe-lines ever published. Though the cost of such equipment is prohibitive on small short lines, such lines may be laid by contractors who own the equipment, and to reduce loss from idle capital during construction even lines of major importance are usually contracted in sections to reliable contractors prepared for such work. Construction was started at seven points on the 420-mile $30,000,000 line into St. Louis.

Compressors.—As gas is the most bulky commodity handled in commerce, it was obvious at the beginning of the natural gas industry that compressors would be necessary. The first compressors were steam driven, but the use of gas-engine driven compressors dates back to 1900.

Extensive refinements in design and materials of large gas engines have gone hand in hand with their increasing use, the most general improvement probably being the universal use of light steel plate or strip type compressor valves. Among the earliest compressor units were some of 5000 h.p., but recent trunk lines use 1000 h.p. units. A few steam-driven compressors are still operated in West Virginia, where gas is more available and compressors are located at the mouth of coal mines. The tendency in long-distance transmission is towards the largest diameter pipe, which can be practically manufactured to stand a pressure of about 400 lbs. (at present about 22 in.), with plenty of compressors. There is no tendency towards pressures of, say, 1,000 lbs and smaller diameter pipe. One of the most recent lines, 450 miles long, is equipped with compressors designed to operate at a ratio of $2\frac{1}{2}$ compressions; that is to say, pressure drop from one station to the next will be from 550 lbs. gauge to 130 lbs. gauge, and there is good engineering thought looking towards ratios as low as $1\frac{1}{4}$.

One company, with a network of lines extending from Central Indiana nearly to New York City, is operating 200,000 h.p. of compressors. The obvious advantages of compression in the natural gas industry are reacting on the manufacturers of gas, causing them to build fewer and larger generating plants and use higher pressure transmission, as has also been done for some time in Germany. A practically continuous system of high-pressure

lines carrying manufactured gas now extends through the territory between St. Louis and Chicago.

The use of large-diameter pipe in long lines, with plenty of compressors, is a remedy for the peaks in consumption. For example, about 65 million cu. ft. of gas is required to raise pressure on 400 miles of 22-in. O.D. pipe from 200 to 400 lbs. gauge.

Diversification of load by gradiated lower rates to large consumers, and to some extent gas holders, are also used. For example, the San Francisco line, with initial capacity of 65 million cu. ft. per day and potential capacity with more compressors of 125 million cu. ft. per day, includes 18 million cu. ft. of holder capacity. While the ratio of gas delivered in the maximum hour to the minimum hour may run 12 to 1, that of maximum hour to average hour is $1\frac{3}{4}$ to 1. On the other hand, the maximum month may have deliveries three times those of the minimum month, but $1\frac{1}{2}$ times the average month. The above ratios are under conditions probably more severe than the average.

By-Products.

Natural Gasoline.—This continues to be the chief by-product, and the production in 1929 is expected to be two billion gallons, with California passing Oklahoma as the leading producer.

An interesting development, so far largely confined to Oklahoma, is the combination gas lift-gasoline recovery plant. It is best suited in principle to wells with little or no back pressure and with a relatively small gas-oil ratio. These conditions existed in the Seminole Field, and compressor capacity of about 750 million ft. daily was used in that district for the joint operation. It resulted in a large increase in production of both oil and natural gasoline at a cost of probably one-third less than the separate operation of gas lift and gasoline recovery plants. It also marked a closer relationship between gasoline recovery and other producing operations than has existed in the past, and gave a concrete illustration of the value of organised operation on engineering principles, rather than separating an operation both in equipment and personnel merely because two different products are attained. If pressure be necessary for flowing wells, and that same pressure will recover natural gasoline, why use absorption for recovering the gasoline?

Analogous, though quite different, and more generally applicable, is the practice of double trapping of gas from wells in California which produce under high back pressure, and the operation of gasoline recovery plants under well pressure. This system is also largely used in West Texas, residue gas from the recovery plants being then burned for carbon black. If a well produced under

300 lbs., why separate the gas at 30 lbs. and recompress it for delivery into long pipe-lines or for re-pressuring depleted oil sands?

Though this seems quite obvious, it is really only rather recently that the intrinsic value of such presure as gas may naturally have has begun to be put to use in producing operations. Much remains to be done in stepping-up pressures and velocities and joining gas production, gasoline recovery, gas lift, re-pressuring, and gas storage in a rational manner with the production of oil which is now beginning to be considered as the liquid phase of the system of hydrocarbons located in place by geological methods. Modern refining practice is beginning to consider all the hydrocarbons together as chemical raw materials, which can only emphasise the logic of considering all their physical properties together in the producing operation.

Carbon Black.—This is second in importance, with 250,000,000 lbs. in 1928, probably increasing in 1929 and the weight of production shifting from Louisiana to Texas. Practically all production is now in these two States, about 600,000,000 being burned for carbon daily in the Panhandle field in Texas. One process is commercially successful in making carbon black by thermal decomposition, but most of the production is still by the old method of burning gas-jets against slowly moving steel surfaces.

Various Chemical Products.—These have a rapidly increasing importance, but, since they are produced by only a few firms, no statistics are available. Also, while of great importance on the marketing end, they utilise only relatively small amounts of natural gas, and on account of the importance of the olefines as chemical raw materials, may even be considered as by-products of cracking rather than of natural gas.

Liquefied Gas Fuels.—Though in use for several years, these will make their first important progress in 1929. Mr. G. G. Oberfel, a prominent person in this trade, estimates that 21,000,000 gallons will be sold in 1929, and that there will be 50,000 domestic consumers. There is available from existing plants 750,000 gallons per day of substantially pure propane, and more than this amount of pure butane, if there be reason for separating it.

The natural gasoline plant residues of about six billion cu. ft. per day contain from 4 to 20 per cent. by volume of propane, or on a conservative average of 6 per cent., 9,500,000 gallons of unrecovered propane daily in gas which is being treated. This may be considered a secondary gas product, being really a by-product of the natural gasoline industry rendered available by development of accurate rectification in the now universally practised stabilising operation.

Propane is sold chiefly for domestic use, being delivered in bulk tank wagons or in cylinders containing generally 100 lbs. at prices ranging from 9 c. to 12 c. per lb. Butane, which so far is sold chiefly by but one important concern, is delivered in 10,000-gallon tank cars for industrial uses, such as gas enrichment and as a high grade gas for ceramic and metallurgic operations. Development this year is the result of the work for a few years back in perfecting high-pressure rectifying columns and equipment for handling, and to the establishment of freight rates and commercial rules for their shipment by rail.

Helium.—This continues to progress, and the discovery of Sir Wm. Ramsay and Lord Rayleigh is now being separated in the new Government plant at Soncy, Texas, at a rate expected to reach 20,000,000 cu. ft. per year, if desired, by the end of 1929, and at a production cost of about $20.00 per thousand. A new discovery of helium-bearing gas is reported from Colorado, and a privately owned plant is being moved from Dexter, Kansas, to this new supply.

PROSPECTS.

Though recent progress is quite encouraging, much opportunity remains. Few people realise the relative amounts of natural gas. For example, gasoline, both straight run and cracked, produced in California refineries in July, 1929, averaged in round figures 281,000 barrels per day, or by weight 73,000,000 lbs. Natural gas produced at the same time, as reported by State authorities, was 1,457,812,000 cu. ft. per day. This gas, on a conservative basis, weighs 87,500,000 lbs.; that is, the weight of gasoline produced in California is but 82½ per cent. of the weight of natural gas produced. The new Kettleman Hills field produces gas weighing more than four times as much as the liquid, largely gasoline, produced with it. An important contribution in progress will be made if petroleum engineers will adopt the custom of occasionally thinking about gas in weights rather than in volumes.

The average price received by the producer for natural gas does not exceed 10 c. per M. of one million B.Th.U. This is selling 100,000 B.Th.U. for a cent. Even at present low prices, 100,000 B.Th.U. as motor fuel sells at the refinery for from 7 to 10 cents.

These figures indicate handsome rewards for hydrogenation or polymerisation processes which will utilise really substantial amounts of gas, converting it into useful materials more susceptible of storage and transportation.

The natural gasoline industry producing liquid equal to 11 per cent. by volume of American motor fuel production is only a good start towards the possibilities that remain.

American Refinery Technology.*

By Benjamin T. Brooks, Ph.D., F.C.S. (Member).

The past year and a half, since the last review number of this Journal, has been characterised, in the refining industry, mainly by more widespread installation of improved distillation equipment, a change which has largely made over most American refineries in the last few years. The preponderating importance of motor fuel and secondarily of lubricants for the 26,000,000 motor vehicles in the United States is, of course, the directing influence in most of the effort at refinery improvement. In 1928 motor fuel yielded 68 per cent. of the income of the petroleum industry. In this work of modernising refinery equipment the rôle of engineering specialists and special equipment manufacturers has been increasingly important. Thus, one of the most active equipment manufacturers, dealing largely with distillation equipment, made their debut in petroleum refining only about five years ago.

In the art of cracking for the production of gasoline there has been a continued prolific output of cracking patents and a continued effort on the part of others to "crack" the patents. The only important litigation thus far decided in this field has been the suit brought by the Universal Oil Products Co. against the Skelly Oil Co. for infringement of the Trumble patent, U.S. Patent 1,281,884, judgment being found for the plaintiff. The judgment of the lower court was sustained by the Court of Appeal. The Skelly Co. operated the Jenkins cracking process.

De Florez[1] has described a new design of cracking still which has been in operation for the last two years, and has demonstrated that it is feasible to build a cracking unit, at moderate cost, which will operate satisfactorily on widely differing charging stocks and under widely varying operation conditions. The De Florez heater eliminates the conventional brick-lined combustion space and makes use of high combustion temperatures, with minimum air excess and no recirculation of flue gases. The combustion chamber is in the form of an upright cylinder carrying a large number of vertical oil heating tubes around the inside wall, thus making use of radiant heat and cooling the flame. Under these conditions there is very little oxidation of the tubes. The combustion gases pass through an air preheater before entering the stack.

* Paper received Jan. 27, 1930.

[1] *Nat. Petr. News*, Dec. 4, 1929. *Oil and Gas J.*, May 2, 1929.

De Florez points out that the terms "vapour phase" and "liquid phase" cracking are misleading, and that these names have come to be applied according to the nature of the ultimate results. The demand for motor fuels having high anti-knock values has led to higher cracking temperatures, and the De Florez equipment apparently has the flexibility to explore the higher temperature range, at various pressures.

The De Florez unit is regularly operated for 600 to 700 stream hours. In the case of heavy crudes the charging stock is introduced

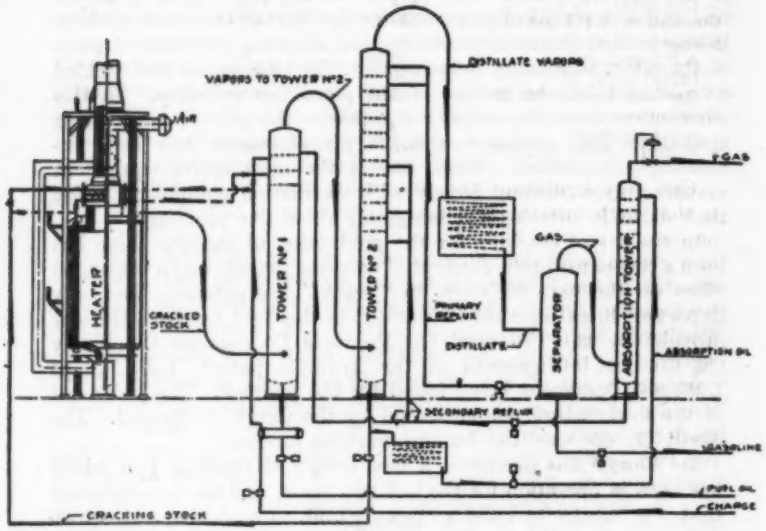

FIG. 1.

TYPICAL FLOW DIAGRAM OF DE FLOREZ CRACKING UNIT.

near the bottom of the fractionating tower, the hot oil and vapours from the heating tubes causing partial distillation of the crude, part going into clean cycle stock and part being drawn off as heavy residuum. In the case of Venezuela crude the over-all fuel consumption has averaged 5 to 6 per cent. of the oil charged, and includes both the gas burned and the small amount of oil fuel used in starting up. On gas oil the fuel consumption is about 12 per cent., but the gasoline yield is about 60 per cent. instead of about 30 per cent. in the case of Venezuela crude. The flow diagram of the De Florez method is shown in the accompanying Fig. 1.

Data reported by De Florez operating at 80lb. pressure and at 1050° to 1100° F. are as follows :—

TABLE I.

	Penn. gas oil.	Calif. gas oil.	Venezuela crude.
Charge, bbls.	1070	1631	1345
Yields—			
Distillate, per cent.	61·40	53·89	36·40
Residuum, per cent.	7·90	18·70	56·00
Gas, per cent.	29·20	26·97	6·10
Distillate—			
A.P.I. gravity	59·5	55·5	55·4
End point, °F.	416	412	403
Circulation, A.P.I. gravity	34·6	28·1	26·3
Charge—			
A.P.I. gravity	40·0	32·4	20·1
Initial b.-pt., °F.	430	456	149
Per cent. over at 392°F.	none	none	8·0
Residuum—			
A.P.I. gravity	7·6	7·2	9·3
Viscosity, furol at 122°F.	280	280	165

One very significant and interesting result of De Florez's work is that high unsaturation and excessive gum formation does not necessarily go with high anti-knock rating. It has long been known in a general way that *pressure* results in cracked gasoline of lower unsaturation and lower gum-forming properties. As is to be expected from earlier work on the relation between yellow colour of cracked distillates, high unsaturation and high gum formation, the result reported in the following table at 100lb. operating pressure is particularly noteworthy. That these results are obtainable without sacrifice of anti-knock value is obviously important. The figure used for anti-knock rating is based on a scale in which straight run Pennsylvania gasoline is taken as zero, and commercial standard anti-knock gasoline at 25 :—

TABLE II.

Effect of Distillate on Character of Distillate.

	15lb. per sq. in.		80lb. per sq. in.		100lb. per sq. in.
A.P.I. gravity	52·7	52·9	52·7	53·8	57·1
Initial b.-pt., °F.	107	104	120	100	98
End point, °F.	397	380	406	390	371
50 per cent. point, °F.	274	276	300	284	248
Colour (Saybolt)	Yellow	Yellow	+7	0	+15
Gum (copper dish)	604	576	—	207	110
Gum (after dilution with equal volume of straight run gasoline)	—	—	—	—	13
Anti-knock rating	32	33	32	33	35

C. R. Wagner has described the results of the "Gyro" process, which is characterised by low-pressure and high-temperature

operation, or "vapour phase."[2] Wagner points out that at the higher temperatures employed in this process that most of the sulphur derivatives are decomposed to hydrogen sulphide, the resulting gasoline having about 50 to 60 per cent. of the organic sulphur that is present in a gasoline made from the same charging stock by the common types of liquid phase cracking. The large-scale operation of this type of process has greatly stimulated the development of chemical processes for the utilisation of the ethylene, propylene and butylenes in the gas. Wagner reports that when operating on gas oil charging stock 25 to 34 per cent. of the charge is converted to gas. One company, now making ethylene glycol from the ethylene produced in this way, operated a trial plant in 1929 for the production of ethyl alcohol, and is reported to be erecting a large commercial plant for this purpose. The interest of the refiner is probably mainly centred in recovering some value for the large amount of gas produced. The utilisation of such gas, very rich in unsaturated hydrocarbons, has brought certain refiners into close co-operation with chemical developments of great interest to the organic chemist.

An interesting process of removing colloidal carbon in cracking still residuum has been developed by Goodwin.[3] Colloidal carbon in this type of oil has often interfered with its sale as fuel oil. In the Goodwin process the oil is treated with a very small proportion of sulphuric acid, not enough to produce sludge. Under the microscope the carbonaceous particles may be seen to gather together in clumps. The oil is passed through a Dorr thickener and about 90 per cent. of the oil is recovered practically free from suspended matter. However, the problem of handling such residuums is of less importance to most refiners since the general adoption of the practice of cutting down the quantity of heavy residuum carried in the reaction chamber, or reducing the time period during which such residuum is held in the reaction chamber.[4] In this way the amount of coke deposited in the chambers has been reduced in most cases to less than ½ lb. per barrel of raw oil charged. The amount of residual oil produced, carrying anywhere from 5 to 25 lb. of suspended carbon per barrel, is still very large, one installation of the Goodwin process treating about 7000 bbls. per day.

Morrell and Faragher[5] have reviewed the corrosion problem in cracking equipment and have given the results obtained by coating the reaction chamber with a ceramic lining made up of furnace cement, sand, water glass and a little short fibre asbestos,

[2] *Nat. Petr. News*, Oct. 30, 1929. *Petroleum Engineer*, Nov., 1929.
[3] *Bull.* 7191, The Dorr Co., New York.
[4] C. W. Nofsinger, *Nat. Petr. News*, Oct. 30, 1929.
[5] *Chem. and Met. Eng.*, 1929, **36**, 596.

followed by a carefully registered period of drying and heating. Whitman and Roberts[6] state that the introduction of lime into the charging stock, in Holmes-Manley cracking stills, reduced the rate of corrosion 89 to 95 per cent. in the stills, 97 per cent. at the pre-heater outlet and 80 per cent. in the bottom of the fractionating tower.

The past year has seen the beginning of three large-scale installations of the high-pressure hydrogenation process, generally known as the Bergius process, as applied to heavy petroleum residual oils. This is the result of an arrangement between the Standard Oil Co. of New Jersey and the I.G. Farbenindustrie, and research by the technologists of the New Jersey Co. since 1927. The larger units are at present under construction and no details of the operation of the development plant at Baton Rouge have been made public, but the *Lamp*, published by the Standard Oil Co. of New Jersey, states that it is possible to convert asphalt or high sulphur crudes or residues to non-asphaltic low sulphur light distillates, and that "The volume yield of gas oil or gasoline is practically 100 per cent."

Cracking and refining by the use of anhydrous aluminium chloride has been very little discussed in recent years probably owing to prolonged litigation over the ownership of the patents. This has finally been settled, however, in favour of the Gulf Refining Co. and A. M. McAfee the inventor. McAfee[7] has published a full description of the methods employed for manufacturing aluminium chloride by methods which permit the sale of this formerly expensive chemical at 5 cents per lb. The aluminium chloride cracking process is employed only for cracking light gas oils, an extensive pressure-cracking plant being operated by the same company for cracking the heavier oils.

Vacuum distillation for lubricating oils has been widely installed in American refineries during the past year. Views of the largest vacuum fractionating tower built up to date are shown in the accompanying photographs. The tower is 18½ ft. inside diam. and 80 ft. high and is designed to process 6,250 bbls. of 50 per cent. reduced crude per day and carries the charging stock to 14 per cent. bottoms. The distillate is fractionated into five closely fractionated streams. The general plan of the unit is shown in the accompanying diagram.

The continued development of aviation has brought about a definite though relatively small demand for lubricating oils of very low pour point. In many chilling plants the use of brine has been

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[6] *Nat. Petr. News*, Dec. 4, 1929.
[7] *Chem. and Met. Eng.*, 1929, **36**, 422.

discontinued in favour of direct ammonia expansion to obtain lower temperatures than are possible with brine. Lederer and Beattie[8] consider that the lowest pour test practically obtainable by centrifuging a 90 viscosity at 210° F. stock is —10° F. This is accomplished by using a special naphtha solvent and chilling to —50° F. The principle cost item in producing low pour tests oils is the power cost for refrigeration. Lederer and Beattie discuss the Weir process, using filter cell, and concludes that as compared with centrifuging, the Weir process is the better in every respect except the recovery of petrolatum. The relatively smaller temperature viscosity coefficient of lubricating oils made from wax-bearing oils as compared with asphalt base oils has been discussed by Wilkin, Oak and Barnard,[9] and more recently by Lederer and Staley[10] who point out that by reduction of the wax content from 0·73 to 0·53 per cent. the "temperature at which the oil changes from a plastic liquid to a plastic solid" is reduced from +10° to −10° F.

The use of solvents other than naphtha for the separation of wax is discussed by J. W. Poole.[11] According to Poole the chief objection to the use of solvents has been the idea that the loss of large proportions of solvent is unavoidable. Poole believes, however, that this can be reduced to as low a figure as 1/5 of 1 per cent., and claims that "with a very small percentage of present refrigeration, or possibly in the colder sections of the United States, with ordinary fresh water cooling, paraffin base lubricating oils of pour tests corresponding to present specifications may be produced." It is interesting to note that of the several solvents which appear to be best suited for this purpose, isopropyl alcohol, acetone and secondary butyl alcohol, are now being manufactured from petroleum.

Refining by liquid sulphur dioxide, though perfected by about 20 years of experimentation and commercial use, has not been extensively adopted, although advocates of the process estimate that lubricating distillates can be refined in this way at a cost of about 8·8 cents per barrel and light oils for about 6·7 cents per barrel.[12]

The continued production of high sulphur crudes, containing hydrogen sulphide or evolving it during distillation, has greatly extended the use of aluminium both in the refinery and in the field. Aluminium heat exchanges have been employed with excellent results and aluminium towers have been advocated.

[8] *Nat. Petr. News*, Dec. 11, 1929.
[9] *Soc. Aut. Eng.*, **1928**, 213.
[10] *Oil & Gas J.*, Mar. 31, 1929.
[11] *Oil and Gas J.*, Sept. 26, 1920.
[12] Brandt, *Chemical Markets*, **1929**, 603.

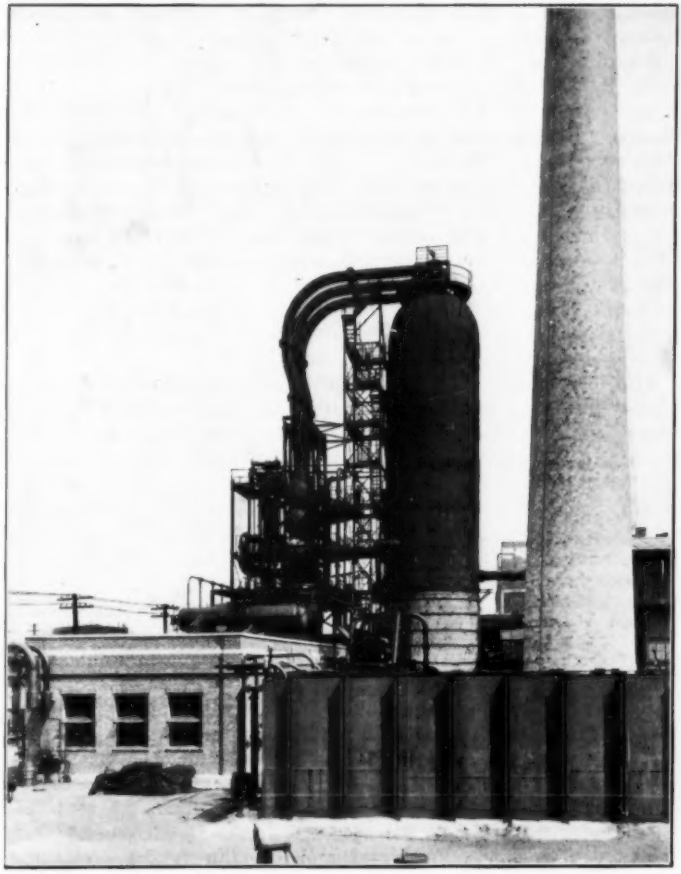

PLATE 1.

LARGE VACUUM STILL FOR LUBRICATING OILS, PROCESSING 6250 BRLS. OF 50 PER CENT. REDUCED CRUDE PER DAY.

Courtesy of the Foster-Wheeler Corporation.

PLATE 2.

DETAIL OF TOWER SHOWN IN PLATE 1 SHOWING ARRANGEMENT FOR TAKING OFF CYLINDER STOCK AND BOTTOMS.

Courtesy of the Foster-Wheeler Corporation.

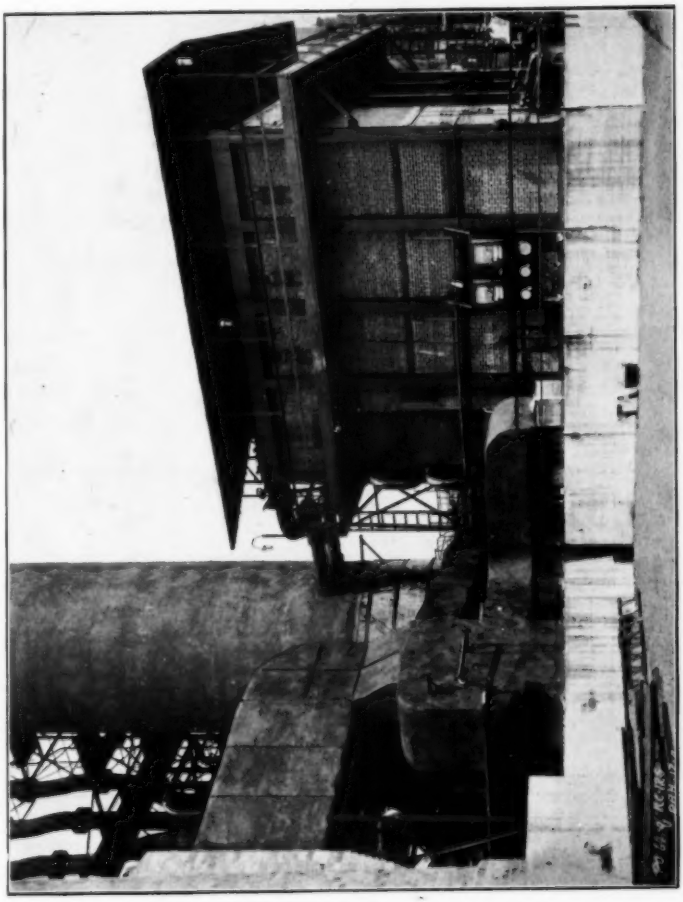

PLATE 3.

SHOWING PIPE STILL USED WITH THE TOWER SHOWN IN PLATE 1.

Courtesy of the Foster-Wheeler Corporation.

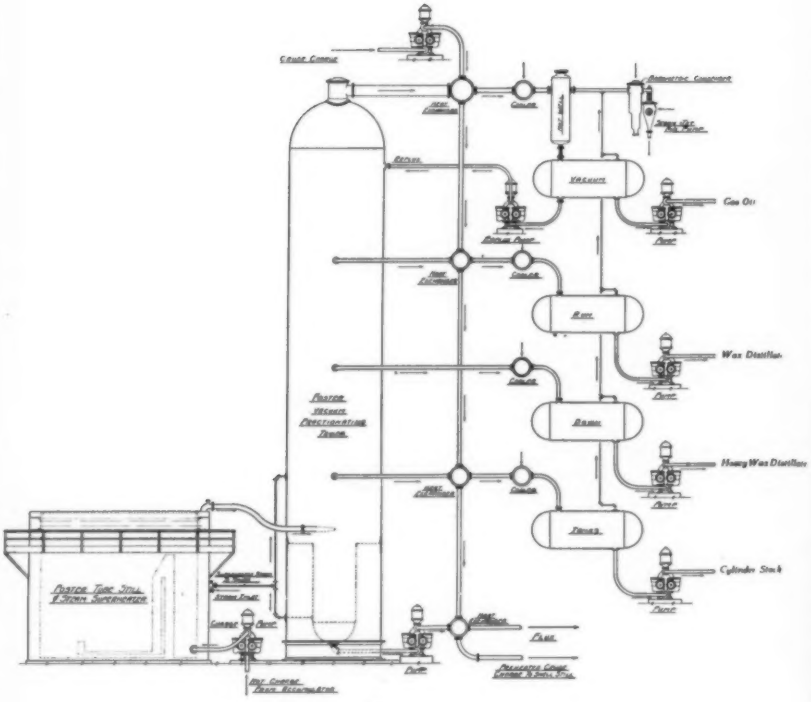

PLATE 4.

FLOW CHART SHOWING DIAGRAMMATICALLY THE ARRANGEMENT OF A COMPLETE FOSTER-WHEELER VACUUM DISTILLATION UNIT WHICH OPERATES IN CONNECTION WITH A SERIES OF TOPPING STILLS.

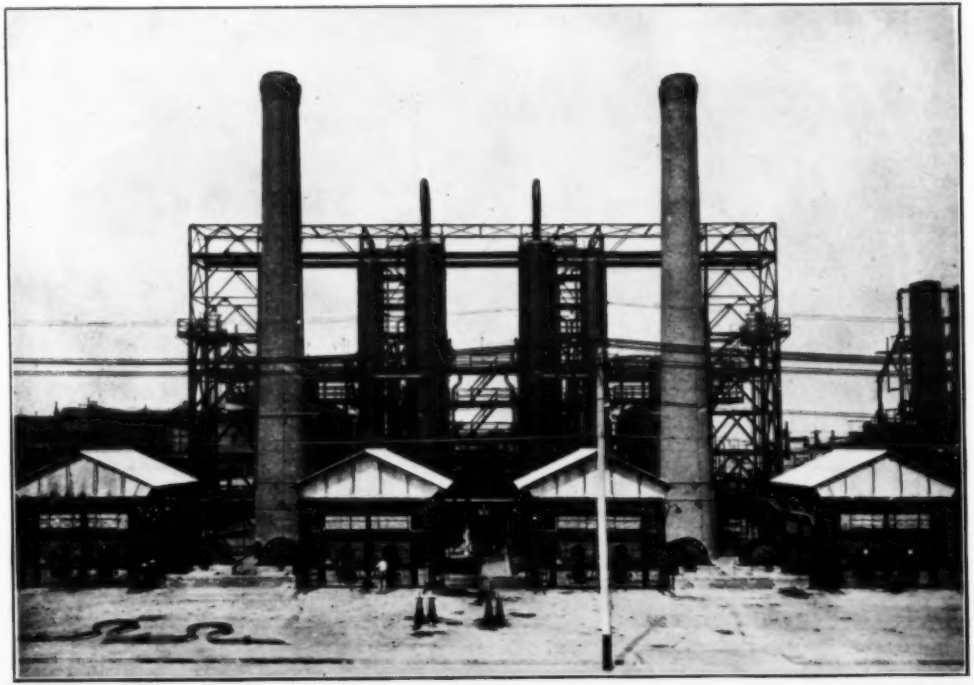

PLATE 5.

ATMOSPHERIC TOPPING AND VACUUM LUBRICATING OIL UNITS OPERATING ON MID-CONTINENT CRUDE.

Courtesy of E. B. Badger and Sons.

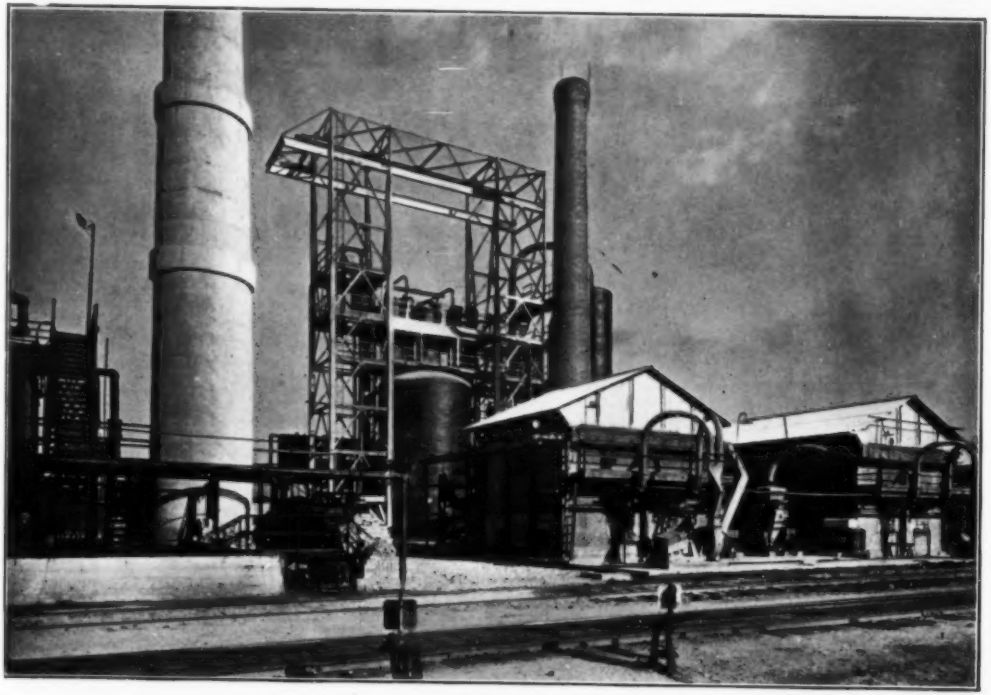

PLATE 6.

ATMOSPHERIC TOPPING AND VACUUM LUBRICATING OIL UNIT OPERATING ON GULF COASTAL CRUDE.

Courtesy of E. B. Badger and Sons.

Courtesy of E. B. Badger and Sons.

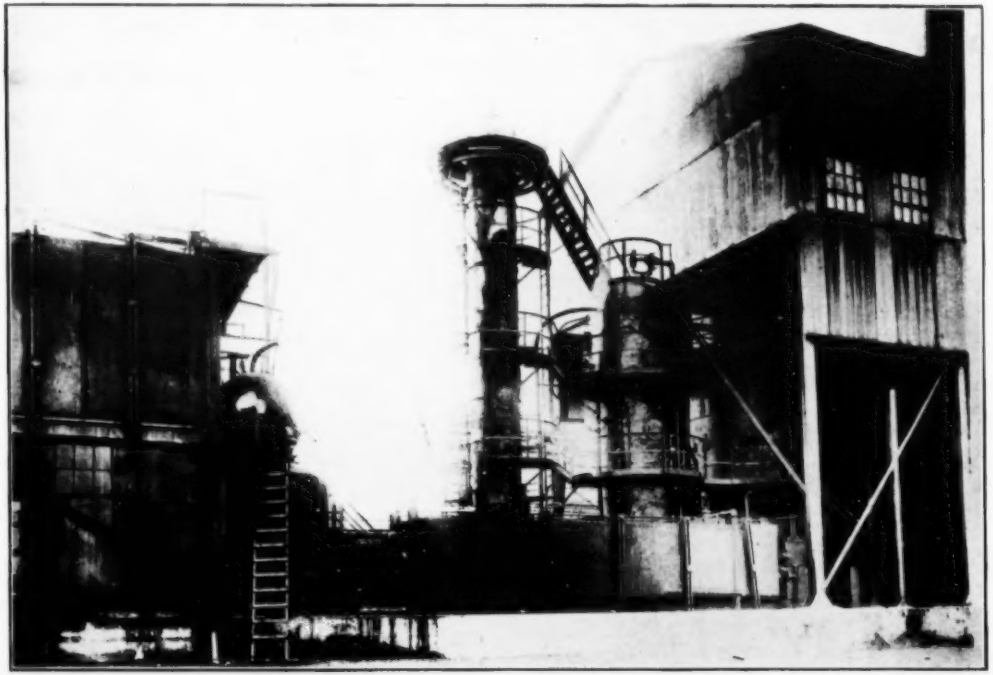

PLATE 7.

THE DE FLOREZ STILL FOR CRACKING AT 1050—1100 F. AT VARIOUS PRESSURES.

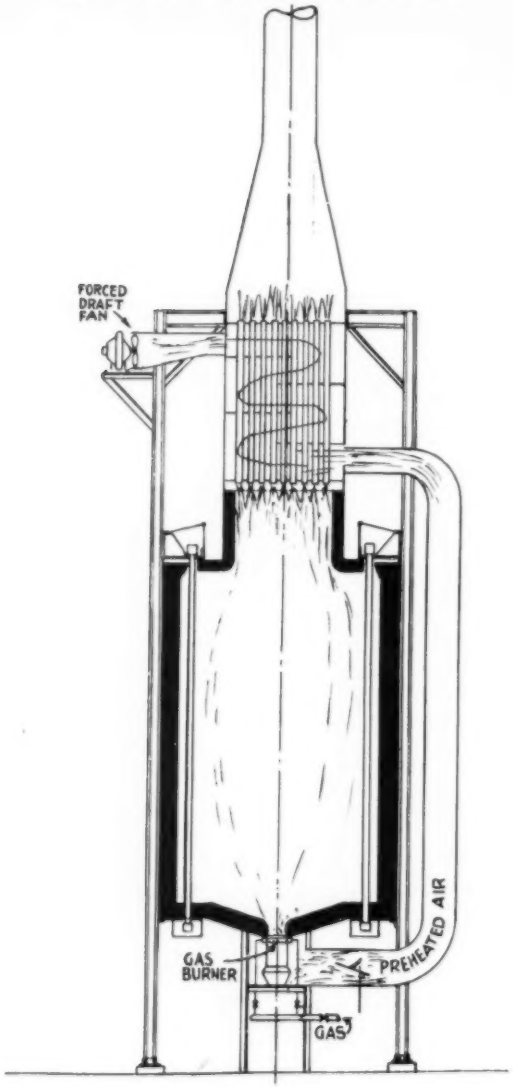

PLATE 8.

DIAGRAM OF DE FLOREZ HEATER SHOWING VERTICAL TUBES IN THE COMBUSTION CHAMBER HEATED BY RADIANT HEAT.

Aluminium tanks have come into use for crudes of this type and aluminium foil has proven to be superior to aluminium paint both as regards resistance to corrosion and preventing evaporation losses by the reflection of heat.

The treatment of crude oil emulsions, while usually more of a field problem than a refinery difficulty, is sometimes a refinery problem of major importance. W. T. Doherty has described an arrangement used successfully by the Humble Oil and Refining Company in which the B.S. is accumulated in 55,000-bbl. storage tanks and treated by salt and a demulsifying agent.[13]

L. C. Uren[14] has reviewed the subject of oil emulsions and emphasised the necessity of studying any particular emulsion before installing treating equipment.

Determinations of physical properties of interest to refinery technologists are found in the work of Bahlke and Kay.[15] on the specific heats of petroleum vapours. The results can be expressed by the empirical equation

$$(1)\ Cp = \frac{4{\cdot}0 - S}{6450}(1{\cdot}8\ t \text{ plus } 702)$$

$$\text{or } (2)\ Cp = \frac{4{\cdot}0 - S}{6450}(t \text{ plus } 670)$$

where Cp=specific heat at atmospheric pressure, S=specific gravity at 15·5° C. (60° F.), and t=° C. in equation (1) or ° F. in equation (2). Copson and Frolich[16] have correlated the work of others on the physical properties of the simpler hydrocarbons, including the pentanes, with values in the lower pressure ranges determined by them.

Probably the most important matter still awaiting satisfactory solution in the natural gas gasoline industry is the utilisation of the potentially enormous volumes of propane and butane which could be produced incidental to the manufacture of gasoline from natural gas. The use of propane as "bottled gas" is rapidly increasing, and one company is shipping it in pressure tank cars, and distributing it in special pressure tank trucks, thus avoiding the shipment of small cylinders. The total amount distributed in 1929, about 14 million gallons, is, however, only a very small fraction of the amount which could be produced in view of the 1½ billion gallons of natural gas gasoline produced. Liquefied

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[13] *Oil and Gas J.*, Aug. 1, 1929.
[14] *Nat. Petr. News*, Mar. 27, 1929, *et seq.*
[15] *Ind. and Eng. Chem.*, 1929, 21, 942.
[16] *Ind. and Eng. Chem.*, 1929, 21, 1116.

propane is very easily produced by high pressure fractionation plants. E. R. Cox[17] has discussed the design and operation of high pressure fractionating columns, and states that towers of thirty trays have proven quite satisfactory. Since the greater the number of trays the less reflux is theoretically required, Cox believes that the most economic construction has not yet been reached and that towers of fifty trays would effect considerable reduction of the cooling and heating required and saving in operating costs. Laboratory control of natural gasoline recovery has been advanced by the analytical methods developed by Podbielniak[18] and by Shepherd.[19]

In the case of gas enrichment by butane and propane, prevailing opinion is that these hydrocarbons can be substituted for gas oil, approximately gallon for gallon, and that at an equal price per gallon the cost of enrichment is about the same.[20] The following data published by Thomas and Setrum[21] is of interest in showing the very narrow boiling-point range of these commercial products produced in quantity, by fractional distillation. Such narrow cuts would not have been considered as commercial possibilities a few years ago.

TABLE III.

Properties of Light Hydrocarbons Used as Liquefied Gases.

	Propane.	Butanes.	Pentanes.
Vapour Pressure, lb. at 70° F.	120	33	9·5 (absol.)
„ 100° F.	195	65	14·3 (absol.)
Sp. gr. of liquid	0·509	0·576	0·630
Initial b.-pt., °F.	—45	12	80
Final b.-pt., °F.	—40	30	100
Wt. per gal. lb.	4·24	4·8	5·25
Cub. ft. gas per gal. liquid	36	32	27
Heating value—			
B.Th.U. per lb.	21,650	21,420	21,130
„ „ gal.	91,800	102,400	110,500

Faragher, Morrell and Essex[22] have given the results of an exhaustive examination of fuel oils including cracking still residuums, and suggest the following formulæ for calculating the calorific value from the gravity :—

(*a*) for straight run dry oil, B.Th.U. per lb. 17,010 plus 90X° A.P.I.

(*b*) for dry cracked residuum, B.Th.U. per lb. 17,654 plus 54X° A.P.I.

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[17] *Refiner and Nat. Gasoline Mfr.*, **1929**, 71.
[18] *Oil and Gas J.*, Nov. 29, 1928.
[19] *Research Paper No.* 75, U.S. Bureau of Standards.
[20] McBride, *Chem. and Met. Eng.*, 1929, **36**, 359.
[21] *Oil and Gas J.*, Oct. 18, 1928.
[22] *Ind. and Eng. Chem.*, 1929, **21**, 933.

Cracking.*

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1. FOREWORD.

THE years 1928 and 1929 showed advance in the cracking art, both in its commercial application and in its technology. Despite the continuing over-production of crude oil beyond the volume required for higher uses, the production of cracked gasoline in the United States increased from 4,250,000,000 gallons in 1927 to 5,140,000,000 gallons in 1928, and an estimated volume of over 6,000,000,000 gallons for 1929. During this period of time a further shifting of attention was noted from the production of maximum gasoline yields to that of anti-knock motor fuel together with by-products such as cracked fuel oil, furnace oil, gas and coke.

In liquid-vapour phase operations, this period has marked the practical slowing down of shell still cracking with more than corresponding increase of large scale pipe still cracking. Pipe still cracking units are in operation converting over 3,000 barrels per day of charge with yields of over 50 per cent. of gasoline, whereas the shell stills treated 125 barrels with gasoline yield of 32 per cent. In the mechanical operation of cracking units, considerable development in regulating devices including arrangements for automatic furnace control, control of liquid flow, and of pressures and temperatures from a central point have been made. Furnaces have been improved by the use of radiant heat, air preheaters, and flue gas recirculation, giving relatively high thermal efficiency with low flue gas temperatures.

Advance in combatting corrosion has been made by lining reaction chambers with cementitious material, the use of alloy steels, chromium plating, and injection of chemicals.

Vapour phase cracking interest has been stimulated by the continued demand for anti-knock motor fuel, but so far has not been a material factor in adding to our cracked motor fuel supply.

Considerable attention has been given to types of cracking such as conversion in the presence of oxygen, or cracking with hydrogenation. Large yields of motor fuel are claimed for the

* Paper received January 14th, 1930.

hydrogenation of heavy oils, and plans are reported for the exploitation of this process.

The conversion of vapour phase still gases into motor fuel has been reported. The cracking of natural gas for the production of benzol and other aromatic and unsaturated hydrocarbons useful for motor fuel has been investigated, and commercial units are under course of construction.

The cracking process developed for petroleum has been found applicable to a variety of other liquid carbonaceous materials, including coal tars, shale-oil, wood tar, fish and vegetable oil.

The terms " liquid-vapour phase " and " vapour phase " cracking are used with no thought that they are strictly accurate terms describing cracking operations, but rather as a convenient basis for rough classification.

2. Liquid-Vapour Phase Cracking.

(a) *Studies of Cracking and Cracked Products.*

H. A. Wilson, in three papers[1], has developed a theory of the cracking of oils on the assumption that they consist largely of paraffin and olefine hydrocarbons and in the cracking unit reach a state of equilibrium. In the first paper, dealing with paraffins alone, he calculates the final composition of the gas and liquid phases in a mixture of paraffins subjected to heat, and states: " The theory has been compared with the results obtained in large scale operations on paraffin oils and appears to give results which agree approximately with the results obtained at temperatures above 600° F." He contends that the addition of hydrogen, methane, or volatile hydrocarbons rich in hydrogen would decrease tar formation in decomposing oil. He also states that maximum amounts of any given hydrocarbon may be obtained by proper choice of temperature and pressure.

In the second paper he calculates the proportion of olefines in a mixture of hydrocarbons resulting from thermal decomposition, and states, " it appears that doubling the pressure should diminish the unsaturated compounds in the vapour to about one-third, while raising the temperature 50° F. should about double them." He believes that while no experimental data on olefine formation are available, if the rate of cracking is small " the liquid and vapour will soon reach approximate equilibrium in accordance with the theory . . . . We should expect the rate of coke formation to be diminished either by raising the pressure or lowering the temperature."

[1] *Proc. Roy. Soc.*, 1927, A116, 501; 1928, A120, 247; 1929, A124, 16.

In the third paper Wilson attempts, from the standpoint of his theory of equilibrium, to point out solutions to a number of practical cracking problems, such as maximum gasoline yields under given conditions of temperature and pressure, the time oil should remain in reaction chambers, operation for maximum throughput or maximum yield, recycling, etc. The papers merit careful study and further experimentation to determine whether their conclusions are valid.

McKee and Parker[2] determined the critical temperatures of gasolines and gas oils with a view to using them to differentiate between liquid and vapour phase cracking. It was found that these oils, though complex mixtures, had definite critical temperatures which could be calculated from the average boiling point as obtained by A.S.T.M. distillation. The work revealed that the critical temperatures of oils used as cracking stock were lower than the temperatures used in some of the commercial liquid-vapour phase cracking processes. Work with mixtures of gas oil and gasoline showed that they followed the rule of Straus and Pawlewski that the critical temperature of a mixture is proportional to its composition by volume. Experiments with solutions of asphaltic material in oil showed that no precipitation took place above the critical temperature, indicating that the asphalt was soluble in the highly compressed vapour.

Sachanen and Tilitscheyew[3] cracked petroleum fractions of narrow boiling points, chiefly of Grosny oils, in a small shell still at final pressures of 61 to 100 atmospheres. Products both lighter and heavier than the charging stocks were produced, though the heavier fractions were not always higher boiling. Cracking appeared to start immediately, when the necessary temperature was reached, without going through an induction period. They report that the velocity of cracking at constant pressure decreased with time. The rate of cracking was lowest for the lightest fractions and gradually increased for heavier substances. "Cracked oils decompose at a slower rate than straight run oils." The velocity of cracking doubled, they claim, for every temperature increase of ten degrees Centigrade between 450 and 475° C. (842–887° F.) and these appeared to be the optimum temperatures. Within the range of 10 to 40 atmospheres, the speed of cracking appeared to be independent of pressure. "In the first stages of cracking oil distillate, coke formation does not take place, and begins only when products of condensation in the form of high specific gravity oils have been formed. The velocity of coke formation increases with increasing time of cracking. It is useless to lower the temperature in order to lessen

[2] *Ind. Eng. Chem.*, 1928, **20**, 1169.
[3] *J. Inst. Petr. Techn.*, 1928, **14**, 761.

coke formation as a certain yield of gasoline always corresponds to a definite yield of coke." Experiments with recycling, starting with a light gas oil, gave 17·5 per cent. of gasoline on one pass, 55 per cent. on four, and after repeated runs the gasoline yield seemed to approach a limit, which was about 60 per cent. with moderate coke formation, or 65 per cent. with considerable coke.

In a further study[4] these investigators reported that in cracking Grosny mixed base fuel oil, increased pressure up to 40 atmospheres increased gas production and decreased heavier distillate. With Surakhany and Baku oils slightly more gasoline was obtained at 10 atmospheres than at higher pressures, but no difference was observed with paraffin wax. The iodine numbers of cracked distillates decreased rapidly with increase of pressure, while aniline points changed in the reverse manner. It was considered that the olefines were in part converted into naphthenes and in part into polymerized products.

Recycling heavier cracked fractions of Grosny and Emba oils, gave progressively lower yields of gasoline and more gas. In the first mild cracking of straight run products it was thought that paraffins are broken up and side chains attached to the aromatic and hydroaromatic hydrocarbons split off, giving comparatively little gas and practically no coke. In heavier cracking or recycling, decomposition of the newly formed simpler aromatic and hydroaromatic hydrocarbons also takes place. This reaction is accompanied by the splitting of side chains at a much lower rate. The high gas yields, they state, are due to liberation of hydrogen and formation of higher hydrocarbons from the separated side chains. The accumulation of aromatic hydrocarbons causes coke formation which takes place during the condensation process. The amount of unsaturated hydrocarbons decreases with each recycling of gas oil. That of aromatics increases rapidly, finally reaching 100 per cent. after the sixth recycling operation. It appears that only three recycling operations are justified when working for high yields of gasoline; the fourth, fifth, and sixth recycling are of value only for aromatic compound production. An independent cracking of gas oil collected from the several recycling operations is recommended, because with increase in the number of the recycling operations higher cracking temperature and longer period of cracking are required for each following cracking.

Sachanen and Tilitscheyew present additional experimental data and endeavour to provide a background of theory for cracking.[5]

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[4] Sachanen and Tilitscheyew, *Neftyanoe Khoz.*, 1929, **16**, 223.

[5] Ber., 1929, **62B**, 658.

They consider the following three reactions possible for the initial stage of the decomposition of paraffin hydrocarbons.

I. $R.CH_2.CH_2.CH_2.R^1 \rightarrow R.CH_3 + CH_2.R^1 + C$,

II. $R.CH_2.CH_2.CH_2.CH_2.R^1 \rightarrow R.CH : CH_2 + CH_2 : CH.R^1 + H_2$,

III. $R.CH_2.CH_2.CH_2.R^1 \rightarrow R.CH : CH_2 + CH_2.R^1$.

Due to hydrogen and carbon not being products of the initial stages of cracking, they assume that the breakdown of paraffins cannot follow either of the first two equations, but must be according to the third, with formation of one molecule of an unsaturated and one of a lower paraffin hydrocarbon. The boiling points of the products obtained lead to the conclusion that the break occurs in the middle of the molecule and that the paraffins formed are the normal hydrocarbons. From the olefines the steps in decomposition are believed to be naphthenes, aromatics and coke. The conditions of cracking will greatly influence these changes, for as a function of pressure, which increases the time factor of cracking, the formation of polymers and naphthenes from the olefines increases. Supporting this, they claim that in the cracking of paraffin, a gasoline produced at 40 atmospheres had but half the iodine number of one produced from the same stock (paraffin) at 10 atmospheres.

To obtain information of value in the study of oil cracking, a number of pure hydrocarbons, di-isoamyl, naphthalene, anthracene, cymene, and tetralin were cracked. The pronounced coke-forming tendency of anthracene, and the production of condensation products but no low-boiling fractions from naphthalene, apparently supported their theory that aromatic substances in cracking stocks are largely responsible for coke formation.

By application of the Nernst heat theorem and of thermochemical data they concluded that paraffins will have the greatest tendency to break near the middle of the chain; that olefines will resist breakdown more than paraffins; while methyl-substituted aromatics will be more stable than those of longer side chains; that hydro-aromatic compounds will dehydrogenate during cracking to aromatics, whereas hydrogen will react with olefines present; and the aromatics formed will undergo condensation to polycyclic substances. The above conclusions they considered were borne out by their experiments.

Sachanen and Tilitscheyew have incorporated the results of their cracking studies in book form, "The Cracking Process in the Liquid Phase."[6]

Butkov[7] cracked oils in an electrically-heated vertical tube with internal metal packing. An Emba solar distillate was cracked at

[6] Moscow-Leningrad, 1928 (in Russian).

[7] *Neftyanoe Khoz.*, 1928, **15**, 674. *Izvestia Teplotch. Inst.* (*Moscow*), 1928, **10**, 7. *Brit. Chem. Abstr.*, B, May 10, 1929, 345.

478–530° C. (892–986° F.) and 0·25 to 4·7 atmospheres with gasoline yields up to 20 per cent. He drew the conclusion that, at the same temperature, pressure decreased the gas and increased the gasoline yield. Decalin (decahydro-naphthalene) and tetralin cracked in the same apparatus gave about 34 and 21 per cent. respectively of products boiling lower than the starting materials. Turpentine also gave gas and low-boiling products.

To characterise the cracking reaction Butkov proposed measuring the change in volume at constant temperature and pressure, or change in pressure at constant volume. In the cracking of cylinder oil in a bomb he found that the rate of increase of dissociation pressure decreased as the experiment went on, and concluded that it approached zero, giving rise to a definite final dissociation pressure for a given temperature. This was thought to correspond to an "equilibrium," though not a strictly chemical one in the literal sense. By applying the van't Hoff reaction isochore, values of the molar heat of dissociation Q_v were calculated. The decomposition was stated to be endothermic, and the heat of dissociation to decrease with increased temperature.

Waterman, with Perquin and van Weston,[8] has continued his studies of the berginisation and cracking of paraffin wax. It was thought that the residues from cracking, which were higher in specific gravity than those from berginisation, were more cyclic in structure.

In a second paper Waterman, te Nuyl, and Perquin[9] follow their previously published comparisons of the low-boiling products of cracking and berginisation with analysis of the fractions boiling above 150° C. (302° F.). The high-boiling materials were fractionated in a cathodic vacuum. In comparing the products from the two processes, they state :—

(*a*) The aniline point on berginisation is about 20° C. (36° F.) higher than on cracking.

(*b*) The refractive index of the cracking products is about 0·02 to 0·03 higher.

(*c*) The bromine value of the cracking products is much higher.

(*d*) The specific weight of the products is higher on cracking.

All these facts indicate the stronger unsaturated, and especially the more cyclic character (aromatic, hydroaromatic, etc.) of the cracking products. On the determination of the bromine number the substitution characterised by the formation of hydrogen bromide is also observed. This substitution was always much more pronounced on cracking than on berginisation. This also indicates the partly aromatic nature of the cracking products.

[8] *J. Inst. Petr. Techn.*, 1928, **14**, 318.
[9] *J. Inst. Petr. Techn.*, 1929, **15**, 369.

They state that the products of berginisation resemble in physical properties the normal paraffin hydrocarbons, although there is an indication of the presence of some unsaturated material. The differences earlier reported between gasoline from berginisation and cracking carry over to the higher boiling products and are more pronounced in the latter.

Phyälä[10], using a special column, carried out slow distillation of Baku oil with a high paraffin content, finding a "first" cracking at 380°–410° C. (716–770° F.), and a "second" at 410–450° C. (770–842° F.).

Carpenter[11] found that Burmah wax (m.p. 58° C. (134° F.) cracked readily in a bomb at 140 lbs. pressure and 418° C. (787° F.) with no coke formation. The fraction boiling to 175° C. (346° F.) contained 19 per cent. unsaturated hydrocarbons, 14 per cent. aromatics, a small percentage of naphthenes, and the rest mostly paraffins. The kerosine cut had an unsaturated content of about 3 per cent. with 12 per cent. aromatics.

Minchin and Nixon[12] cracked Burmah paraffin at 450–455° C. (842–851° F.) and a pressure of 100 lbs.

Hugel and Artichevitch[13] cracked hexadecane and hexadecene in an electrically heated steel tube, preferably in the gas phase, under pressures up to 1,000 atmospheres. With the unsaturated compound the carbon chain seemed to break near the double bond, to form a saturated radical which gave paraffinic substances, and an unsaturated radical polymerising to oily products. The cracking of hexadecene took place at lower temperature as pressure was increased, up to a certain limit.

Hexadecane underwent about 15 per cent. decomposition during 24 hrs. heating at 400° C. (752° F.) under 500 atms. At 470° C. (878° F.) 60 per cent. was converted into lower boiling products and at the same time higher boiling liquids equivalent to about 15 per cent. by weight of the hydrocarbon were formed.

Dunstan and Pitkethly[14] describe an apparatus in which small amounts of oil are heated in a silica tube maintained over mercury at pressures up to 1000 lb. per sq. in. and visual observation of its behaviour were made.

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[10] *Tekniska Föreningens i Finland Förhandlingar*, 1928, **48**, 221. *Chem. Abstr.*, 1929, **23**, 1499.

[11] *J. Inst. Petr. Techn.*, 1928, **14**, 446; see page 460.

[12] *J. Inst. Petr. Techn.*, 1928, **14**, 477.

[13] *Ann. Off. Nat. Comb. Liquides*, 1928, **3**, 985.

[14] *Ind. Eng. Chem.*, 1929, **21**, 646.

Several investigators have studied the chemical constitution of cracked oils. Roseanu[16] stated that at cracking temperatures of 230°–360° C. (446°–500° F.) " terpenic " hydrocarbons are produced which at a temperature of 400° C. (752° F.) go over to aromatics. At temperatures above 500° C. (932° F.) the process of forming benzene hydrocarbons is said to be reversible, and when maximum temperatures are passed, at certain pressures, more gas than light gasoline hydrocarbons or more heavy hydrocarbons than light are formed. From the incomplete researches made thus far it was possible to identify several aromatic hydrocarbons in cracked gasoline by the melting point of the picrates. Benzene and some of its homologues, mesitylene, pseudocumene, indene, fluorene, terpenic compounds, triphenyl-naphthalenes and naphthalene in considerable quantity were found in the cracked product. Oil of turpentine, having a specific gravity of 0·856 and a boiling point of 160° C. (320° F.) when passed through a red-hot iron tube is converted to isoprene, m-xylol, naphthalene, anthracene, that is, to a product having almost the same properties as the terpenic hydrocarbons obtained by cracking, and one which may be regarded as a transition stage between the naphthenic hydrocarbons of heavy oils and the aromatics of the cracked oil.

Garner[17] has made a critical study of the determination of aromatic, olefine, naphthene and paraffin hydrocarbons in cracked gasoline.

Smirnow[18] has developed a method of determining olefines in cracked distillates by measurement of the volume reacting with liquid nitric-oxide at —15° to —20° C. (+5 to +4° F.).

By a system of fractional extraction McKittrick[19] succeeded in isolating sulphur compounds from cracked naphtha. He concluded that of the total thiophene sulphur present 1 per cent. was thiophene, 7 per cent. thiotolene, and 15 per cent. thioxene isomers, with 77 per cent. higher boiling. The sulphur compounds in the sludge from the low temperature refining of cracked naphtha proved to be sulphides, apparently cyclic.

(*b*) *Cracking of Specific Oils.*

1. *Petroleum Oils.*—Egloff[20] showed that high pressure is not necessary in the cracking of light oils. In present commercial practice a charging stock of 39·0° A.P.I. gravity with initial boiling

[16] *Mon. petrole roumain*, 1929, **29**, 115.
[17] *J. Inst. Petr. Techn.*, 1928, **14**, 695.
[18] *Neftyanoe Khoz.*, 1928, **15**, 217.
[19] *Ind. Eng. Chem.*, 1929, **21**, 585.
[20] *Oil Gas J.*, Mar. 7, 1929, 151. *Petroleum Z.*, 1929, **25**, 507. *Petroleum Times*, 1929, **21**, 457.

point of 350° F. (177° C.) and end boiling point 732°F. (389° C.) is being cracked at 220 lb. pressure and a liquid temperature of 915° F. (490° C.) to yield over 68 per cent. of gasoline.

Faragher and Morrell[21] cracked four West Texas topped crudes at pressures of 125–150 lb. per sq. in. obtaining yields of 60 per cent. of gasoline or 44 per cent. based on the original crude oil. Should the pressure distillate bottoms be recycled, the yields could be increased to 57·5 per cent. on the topped crude, or 49·5 per cent. on the crude oil. The ultimate yield of gasoline by topping and cracking by the non-residuum method amounted to 75 per cent. Residuum operation gave 53 per cent. of gasoline and 31 per cent. of fuel oil. The anti-knock value of the cracked gasoline varied from 35 to 43 per cent. benzol equivalent in Pennsylvania straight run gasoline.

Born[22] cracked topped crude from Pecos County, Texas, obtaining 45·4 per cent. cracked gasoline, or 49·4 per cent. when pressure distillate bottoms were recycled. A heavy fuel oil gave 41 per cent. cracked gasoline.

The cracking of Dundee (Muskegon, Michigan Field) topped crude at 200 lb. pressure gave 70 per cent. gasoline according to Faragher and Morrell.[23] Reduced crude from which kerosine distillate as well as gasoline had been removed, when cracked in non-residuum operation at 125 lb. gave 61 per cent. gasoline. Treatment with acid and plumbite produced a sweet product, low in sulphur and gum. The anti-knock value of the gasoline was poor.

Francis[24] reports the cracking of a heavy gas oil and heavy bottoms from Winkler County, Texas, crude. The gas oil was blended with 1½ lb. per barrel of hydrated lime and cracked at 780°–820° F. (471°–438° C.) under 150–165 lb. pressure. A yield of 60 per cent. of pressure distillate was obtained, of which 58 per cent. was gasoline.

Hashimoto[25] reported on the cracking of California and Japanese crudes in Japan by the Dubbs process and Cross and Jenkins installations.

Phyälä[26] found that a large part of the paraffins and asphalts in residues from Grosny, Tscheleken, and Surachany petroleums decomposed during rapid distillation at 380°–450° C. (716°–842° F.)

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[21] *Oil Gas J.*, July 19, 1928, 34.
[22] *Oil Gas J.*, Dec. 6, 1928, 224. *Refiner Nat. Gasoline Mfg.*, Apr., 1929, 67.
[23] *Oil Gas J.*, Apr. 25, 1929, 108.
[24] *Oil Gas J.*, Mar. 7, 1929, 147.
[25] *Trans. Fuel Conference, World Power Conference, London*, 1928, I, 553. *Petr. Times*, 1928, **20**, 542.
[26] *Petroleum Z.*, 1928, **24**, 308.

without yielding pitch or coke. In one instance 71 per cent. of the paraffin and 90 per cent. of the asphalt were so decomposed.

Sachanov and Tilitscheyew[27] carried out an extensive investigation of the cracking of heavy Russian oils and residues, with a view to determining whether commercial application of cracking in the case of these oils was economically sound. They cracked oils at 425° C. (797° F.) in a shell still up to 50 atm. pressure, operating either by light cracking to reduce the viscosity, medium cracking to give gasoline and marketable fuel oil, or heavy cracking to yield gasoline and coke. With Grosny paraffin base fuel oil, which is produced in large amounts and because of its high cold test is difficult to transport, light cracking gave a satisfactory reduction in viscosity, while medium cracking produced an acceptable fuel oil in yield of 65 per cent. and with recycling 30 per cent. of gasoline (by weight). "The yields of cracked gasoline and kerosine are independent of the pressure even when varied in wide range from 10 to 40 atm." Heavy cracking gave 57 per cent. of gasoline and 14 per cent. coke. Surachany mazout yielded up to 65 per cent. coke. A considerable number of other Russian residues and heavy oils were cracked. Some gave so much coke that only light cracking was feasible. The gasolines from paraffin base distillate and Grosny and Surachany residues were light in colour and less gummy than the gasolines which were formed from heavy crudes and tars.

The same investigators[28] cracked Emba solar oils and recracked the recycle stock until four cracking operations had been performed. A light cracking stock gave 40 per cent. gasoline on once-through cracking, and 58 per cent. with recycling. It was found that in all cases more than 50 per cent. of the total gasoline produced was obtained in the first cracking. The first recycle gave less than 25 per cent. of the total and cracking of the third recycle stock gave less than 5 per cent. of the total gasoline, the cracking of recycle material being accompanied by proportionally greater gas formation. Cracking was carried out at 450° C. (842° F.) and 40 atm. pressure.

Roseanu[29] cracked Rumanian residues in Dubbs units to obtain a good yield of gasoline.

Tilitscheyew[30] reported a laboratory study of the cracking of Ural topped crude.

Gerr[31] obtained gasolines of high anti-knock quality containing up

[27] *Neftyanoe Khoz.*, 1928, **15**, 328.
[28] *Neftyanoe Khoz.*, 1929, **16**, 62.
[29] *Mon. petrole roumain*, 1928, **28**, 2075.
[30] *Neftyanoe Khoz.*, 1929, **16**, 82.
[31] *Neftyanoe Khoz.*, 1928, **15**, 343.

to 25 per cent. of aromatic hydrocarbons by cracking Surachany crude oil and Baku kerosine distillate at atmospheric pressure both on a plant and laboratory scale. Similar results were reported in laboratory tests on paraffin wax, Surachany fuel oil, and cracked kerosine. The temperature range 670°-700°C. (1238°-1292°F.) gave the highest yield of aromatic compounds.

Sachanen and Bestuschew[32] cracked Balachany mazout at 425°C. (815°F.) and 15 atm. in a small shell still and determined the properties of the cracked residue and of the oil distilled from the residue in vacuum. The cracked distillate differed from fractions of the original oil. Its solidifying point was higher except where the cracking had been of long duration. The oil was composed mainly of aromatic and hydro-aromatic hydrocarbons.

2. *Non-petroleum Oils.*—The cracking process used for petroleum has been found applicable to the conversion of oils from a variety of other sources.

Gavin[33] states that the oil from shale distillation may give a yield, by a combination of topping and cracking, of from 52 to 64 per cent. of gasoline. He finds that the cracked product is more easily refined than the straight run fraction.

Egloff[34] reports results of cracking American, Scotch, Australian, French, and Esthonian shale-oils showing yields of 40 to 55 per cent. gasoline.

Gilmore, Rosewarne, and Swinnerton[35] claim that pressure cracking tests upon crude Canadian shale-oil yield 60 to 65 per cent. gasoline, and bitumen from tar sands showed 40 per cent. gasoline.

Egloff[34, 36] finds that the cracking of low temperature coal tars produces motor fuel of high anti-knock property in yields of 22 to 24 per cent. on a tar acid free basis, and, in addition to the fuel oil, gas and coke products, useful tar acids of low boiling-point. The coal tars were derived from West Virginia, Ohio, Indiana, and Utah coals. Pressures of about 100 lbs. and temperatures of 435°C. (815°F.) to 452°C. (845°F.) were used. A neutral oil distillate (free from tar, acids, and pitch) from the carbonisation of West Virginia bituminous coal gave more than 50 per cent. gasoline.

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[32] *Petroleum Z.*, 1929, **25**, 1307.

[33] *Ind. Eng. Chem.*, 1928, **20**, 784.

[34] *Trans. Fuel Conference, World Power Conference, London*, **1928**, I, 763.

[35] *Canadian Dept. of Mines, Mines Branch*, No. **689**, 121 (1928); see also Clark, *Alberta Sci. Ind. Research Council Rept. No.* 18 (1929).

[36] *Petroleum Z.*, 1929, **25**, 573.

Dunstan[37] reported the cracking of a number of low temperature carbonisation tars with yields of 8 to 12 per cent. boiling within motor fuel range when using temperatures of about 450°C. (842°F.) and 160 lbs. pressure. He stated, "Low temperature tar distillates are inferior cracking stock and the possibilities of utilising them for such purposes on a commercial scale, bearing in mind the difficulty of separating and disposing of the tar acids, would be problematic."

Egloff[38] stated that a German lignite tar cracked at 438°C. (820°F.) at 90 lbs. pressure gave 38 per cent. gasoline after refining out the tar acids and bases, while a distillate oil at 150 lbs. and 454°C. (850°F.) gave 47 per cent. gasoline.

Mailhe[39] reported that heating lignite wax with zinc chloride at 440°C. (824°F.) yields about 50 per cent. of liquid hydrocarbon.

Morrell and Faragher[40] cracked oil from cannel coal at 125 lbs. pressure and obtained 39 per cent. of tar acid and base free motor fuel, or 49 per cent. with recycling of pressure distillate bottoms.

By cracking high boiling tar acids from coal at 785° to 800°F. (419°-428°C.) under 40 to 75 lbs. pressure, Morrell and Egloff[41] obtained on the average 23 per cent. of tar acids of low boiling-point.

Morrell and Egloff[42] subjected tar derived from the retorting of Douglas fir wood to cracking under pressures of 75 to 120 lbs. and temperatures of 393° to 405°C. Approximately 33 per cent. of motor fuel was obtained of higher anti-knock value than benzene. Pine tar oils gave a yield of distillate by cracking of from 22 to 41 per cent. The cracking of tars from hickory and oak at 720°F. under 90 lbs. pressure yielded approximately 24 per cent. of high anti-knock motor fuel.

Ipatiew and Petrov[43] heated wood tar under pressure in the presence of oxides of iron and aluminium with or without hydrogen being present. The most favourable condition for the formation of liquid products was an excess of hydrogen in the presence of catalyst at 440°-460°C.

Egloff[44] reports the obtaining of over 60 per cent. of motor fuel from palm and cotton seed oil and 45 per cent. from Menhaden fish oil.

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[37] *Proc. Second Intern. Conference Bituminous Coal*, **1928**, I, 210.
[38] *Trans. Fuel Conference, World Power Conference, London*, **1928**, I, 763.
[39] *J. usine gaz.*, 1928, **52**, 132.
[40] *Amer. Chem. Soc., Columbus Meeting, Apr.*, 1929.
[41] *Proc. Second Intern. Conference Bituminous Coal*, 1928, II, 580.
[42] *Ind. Eng. Chem.*, 43 *Ber.*, 1929, **62**, 401, 1929, **21**, 537.
[43] *Ber.*, 1929, **62**, 401,
[44] *Trans. Fuel Conference, World Power Conference, London*, 1928, I, 763.

UNITED STATES PATENTS.

GUSTAV EGLOFF and H. P. BENNER (U.S.P. 1,688,859, Oct. 23, 1928) patent

"A process of cracking hydrocarbons, consisting in dispersing in a liquid hydrocarbon oil not less than 10 per cent. by volume or over 60 per cent. by volume of a solid bitumen in colloidal form, and in then subjecting the mixture to a cracking temperature while the same is maintained under a superatmospheric pressure, to cause substantial vaporisation, subjecting the vapours to reflux condensation returning the reflux condensate to be treated and condensing the uncondensed vapours."

W. H. HAMPTON (U.S.P. 1,687,763, Oct. 16, 1928) presents the

"Process of obtaining valuable products from shale like bituminiferous solids which comprises digesting such a shale-like bituminiferous solid in finely divided condition with a heavy mineral oil at temperatures between 500° and 700° F., mixing steam with the evolved vapours and subjecting the mixture to cracking treatment at higher temperatures, fractionally condensing the products of cracking, diluting the residual digestion mixture with a lighter oil, separating solid matter from the diluted mixture, treating the residual oil to obtain a heavy fraction therefrom, and utilising such heavy fraction and a heavy fraction obtained from the aforesaid cracking products for digestion of a further portion of shale or other bituminiferous solid."

M. J. TRUMBLE (U.S.P. 1,714,963, May 28, 1929) claims

"A process for treating solid bituminous material for the extraction of volatiles which comprises: subjecting a condensate from the distillation of solid bituminous material to a cracking process in a cracking still; recovering hot carbon resulting from said cracking process in a receptacle separate from said cracking still; passing superheated steam and hot vapours coming from said cracking process and said carbon receptacle respectively through a body of solid bituminous material for distilling volatiles from said bituminous material; dephlegmating the vapours resulting from said distillation; delivering the condensate resulting from said dephlegmation to said cracking process; and subjecting the uncondensed vapours resulting from said dephlegmation to a condensing process."

(c) *Descriptions of Liquid-Vapour Phase Cracking.*

After a general discussion of cracking, Dunstan and Pitkethly[45] take up the Beale, Coxon, and Dunstan invention (U.S.P. 1,708,782, April 9, 1929) by which the formation of coke in cracking is minimised by keeping the oil in a highly turbulent motion resulting from surges and reciprocating action imparted by a pump as the oil moves forward through the heating coil. This device is stated to make enlarged reaction chambers unnecessary. The process operating, at a temperature of 450° C. and pressure of 600 lb., on a Persian residue yields about 25 per cent. of motor spirit and a fuel oil free from carbon.

[45] *Ind. Eng. Chem.*, 1929, 21, 643; see *Petr. Times*, 1928, 20, 329.

Truesdell[46] has described the tube and tank units of the Standard Oil Co. of Ohio which are designed to operate at pressures of 1,500 lb. and temperatures of 1,000° F. Three soaking drums are used on each two cracking units, the extra drum allowing continuous operations without stopping for clean-out of the chamber. The furnace tubes are of chrome-nickel-iron. Pressures of 1,000 to 1,100 lb. on the coil, and 650 to 750 lb. on the reaction chamber are used. Gasoline yields of 62 per cent. on gas oil charging stock have been reported.

Egloff[47] discusses the operation of a modern cracking process. He stresses its flexibility, allowing operation for light cracking of heavy oils to reduce viscosity, cracking for gasoline and residual oils, or for gasoline and coke. Yields of gasoline from a variety of charging stocks are given, with yields and properties of the residual oil, coke, and gas.

Truesdell[48] and Hovey[49] describe the combination of a Cross installation and skimming plant at the refinery of the Waverly Oil Works, Pittsburg.

In the cracking plant of the Indian Refining Co., Lawrenceville, Illinois,[50] recycle stock is not returned to the unit from which it was produced, but is passed through another unit operating at higher temperature and pressure.

Ziegenhain[51] states that an increased amount of light distillate and fuel oil of low viscosity are obtained in West Texas and Panhandle refineries which have no "cracking plants," by partially cracking the residuum from the crude batteries at a temperature of 1,000 to 1,200° F. Use of tubes of small diameter minimises the formation and deposition of coke. The cracked oil is shock-chilled 50 to 100° upon entering the tower by directing upon it the "knockdown" of the tower. Based on the residuum charged, 10 per cent. of gasoline and about 78 per cent. of fuel oil of low viscosity, low pour point, and high B.Th.U. content were obtained.

Leach[52] points out the economies which heat exchangers have introduced in cracking still operation.

Nofsinger[53] states that topped crude to be cracked may either be charged directly to a mixing tank and converted with recycle stock, or it may be cracked lightly in an auxiliary coil and discharged into the evaporator, the fuel oil dropping out and gas oil being

[46] *Nat. Petr. News*, Apr. 3, 1929, 74; June 26, 1929, 78; Aug. 28, 1929, 70.
[47] *Trans. Fuel Conference, World Power Conference, London*, 1928, I, 763.
[48] *Nat. Petr. News*, Mar. 13, 1929, 69.
[49] *Oil Gas J.*, Oct. 10, 1929, 141.
[50] *Ref. and Nat. Gas. Mfr.*, Nov., 1928, 60.
[51] *Oil Gas J.*, May 24, 1929, 165.
[52] *Nat. Petr. News*, Oct. 30, 1929, 162.
[53] *Nat. Petr. News*, Oct. 30, 1929, 153.

vaporised and condensed in the bubble tower with the recycle stock. The latter method of operation increases the operating time of cracking.

Hargrove[54] outlines a cracking operation with an auxiliary coil or "viscosity breaker."

Jasper[55] discusses the design of pressure vessels for the oil industry. He states that on account of the stresses to be borne, plain carbon steel is preferable to alloy steel. The head which will give the greatest strength is ellipsoidal in shape. This design is preferable to the ordinary dished head.

Mekler[56] describes a number of furnaces suitable for cracking stills, both of the convection and radiant heat types, some including recirculation of flue gases.

Keyes[57] describes systems of fractionation for vapours and for crude residual tar from cracking units. The vapours to be fractionated are passed through a coil in the lower part of the bubble tower before discharging therein at an intermediate point.

It is is also claimed that careful fractionation of gas oil charging stock, dropping out tarry matter, asphalt, etc., is desirable to reduce coke formation in the cracking zone.[58]

The Vickers Co.[59] is reported to propose improvements in its cracking equipment in Grozny and Baku by which the fuel oil will be moderately heated in a first coil and the gas oil fraction as well as a part of the lubricant cut distilled out. In a second coil the bottoms will be cracked together with the gas oil after this has been sent through the fractionating tower handling the cracked gasoline.

Bender[60] describes the Carburol cracking set up, which handles heavy as well as light oils. Yields of crude cracked gasoline reported range from 46 per cent. on residues to 78 per cent. on gas oil.

Tregubov[61] describes the cracking of residues in a "Kvitko cracking still," a shell still operating at 420 to 430° C. and 5 atms. pressure.

Obryadchikov[62] discusses the design of cracking furnaces to allow not only for vaporising the oil, but also to furnish heat for

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[54] *Nat. Petr. News*, May 1, 1929, 77.
[55] *Oil Gas J.*, June 14, 1928, 123.
[56] *Fuels and Furnaces*, 1928, **6**, 1073.
[57] *Chem. Met. Eng.*, 1929, **36**, 78; *Nat. Petr. News*, Mar. 13, 1929, 78.
[58] *Nat. Petr. News*, Sept. 11, 1929, 89.
[59] *Neftyanoe Khoz.*, 1929, **16**, 101.
[60] *Petroleum Z.*, 1929, **25**, 1187.
[61] *Proc. of the First All-Russian Scientific Tech. Mining Congress*, 1926, **5**, 42 (1928); *Chem. Abstr.*, 1929, **23**, 2283.
[62] *Neftyanoe Khoz.*, 1929, **16**, 357.

cracking, which is assumed to be endothermic, following Leslie and Pothoff,[63] and Sakhanen and Tilitscheyew.[64]

Zotos[65] stresses the importance of heat transfer in heating oils to be cracked and predicts an increased use of indirect heating, as by a metal bath, to avoid over-heating of surface films on the inside of the tubes.

PATENTS.

Processes and Apparatus for Liquid-Vapour Phase Cracking.

UNITED STATES PATENTS.

J. G. Alther (U.S.P. 1,685,476, Sept. 25, 1928) claims

"The process of cracking petroleum oil, which consists in passing oil in a stream of progressively decreasing size, through a heating zone of progressively decreasing temperature, in transferring the oil while in the smallest stream to a vapour chamber, and in removing vapours from said chamber."

S. J. M. Auld, A. E. Dunstan, and P. H. Herring (U.S.P. 1,711,219, Apr. 30, 1929) describe

"An apparatus for use in the pressure cracking of liquid hydrocarbons, comprising a pre-heater, a plurality of separate and relatively short thermalising tubes into which the liquid passes from the pre-heater, a reactor surmounting the thermalising tubes and into which the liquid issues therefrom, a setting within which the said elements are mounted, the setting comprising a flue within which the thermalising tubes are disposed, and means for the regulation of the application of heat to the said thermalising tubes, comprising a wall adjacent the said flue, a series of valves within the said wall, and means for the operation of the said valves externally of the setting."

E. S. L. Beale, G. H. Coxon, and A. E. Dunstan (U.S.P. 1,708,782, Apr. 9, 1929) present

"A process for the cracking of hydrocarbon liquids, comprising imparting to the liquid to be cracked a predominant feed flow in a stream through an elongated passage of restricted cross section, imparting a cracking temperature to the stream of liquid in its passage, and imposing upon the liquid in its passage impulses alternating in opposite directions to effect substantial alternately reciprocating movement of the liquid in addition to its predominant feed flow through the restricted passage."

E. S. L. Beale, G. H. Coxon, and A. E. Dunstan (U.S.P. 1,708,782, Apr. 9, 1929) present

"The column of oil within the coil had imparted to it a velocity of about 12 feet per second alternately in opposite directions under conditions in which water hammer was avoided, and the feed flow of the oil was only 1/30th to 1/20th feet per second. The temperature of the

[63] *Ind. Eng. Chem*, 1926, **18**, 776.
[64] *J. Chim. Promys.* (*Moscow*), 1927, IV, 516.
[65] *Petroleum Z.*, 1929, **25**, 503.

oil at the end of the fourth tube from the lowest in the coil was maintained at about 380° C., at the end of the fifth tube at about 450° C., at the end of the sixth tube at about 440° C., at the end of the seventh tube at about 400° C., and at the end of the first cooler tube at about 250° C.

"Thus in an experimental apparatus a Persian gas oil was treated and a yield of motor spirit from 23 to 25 per cent. boiling below 200° C. was obtained with a production of less than 0·25 per cent. of coke; and a Persian 65 per cent. residue was treated and a yield of 15 per cent. motor spirit boiling below 200° C. was obtained with a production of less than 0·25 per cent. of coke."

C. B. Belknap (U.S.P. 1,704,277, Mar. 5, 1929) covers

"An apparatus for treating oils, the combination with means for mechanically placing the oil, while in a liquid state, under a pre-determined pressure, means for heating the oil while in a liquid state, said first means being arranged to prevent the generation of vapours until after the oil has been heated in a liquid state under a pre-determined pressure and means thereafter for providing a vapour space adjacent the oil in the liquid state, to receive the vapours generated."

J. E. Bell (U.S.P. 1,688,325, Oct. 23, 1928) presents

"The improvement in the operation of externally heated pressure stills for cracking hydrocarbon oils, which comprises circulating oil from a bulk supply drum to the lower end of vertically arranged heating tubes and thence upwardly through the heating tubes and back to the bulk supply drum from the upper end of the heating tubes, heating the oil to the cracking temperature in the heating tubes by passing heating gases first in contact with the upper end of the heating tubes and then downwardly over the heating tubes and progressively increasing the velocity of flow of the heating gases as their temperature declines, whereby uniform distribution of the heat absorption is promoted and the oil is brought to the maximum cracking temperature as it leaves the heating tubes and is discharged to the bulk supply drum."

J. E. Bell (U.S.P. 1,693,946, Dec. 4, 1928) presents

"The improvement in the operation of pressure stills for cracking hydrocarbon oils and distillates, which comprises subjecting the vapours from the still to a refluxing operation in a zone separate from the vaporising zone in direct contact with fresh charging stock to the still, returning the reflux and unvaporised charging stock introduced into the refluxing operation to that portion of the still stock which is to be immediately subjected to high temperature, subjecting the vapours from the refluxing operation to a fractional condensation in indirect heat exchanging relation with fresh charging stock and introducing the fresh charging stock so preheated directly to the pressure still."

Otto Behimer (U.S.P. 1,709,302, Apr. 16, 1929) presents

"Apparatus for treating hydrocarbon oils comprising a charging line, a pump for forcing oil through the charging line, means for heating the oil in transit, a still wherein distillation of the heated oil is effected, a fractionating tower for separating the vapours evolved in the still, a surge pump having a surge line for pumping the hot condensate from the fractionating tower back to the heating means, and means for positively introducing a cooling medium into the surge line of the surge pump to maintain the liquid therein cooler than the oil being pumped."

J. C. BLACK (U.S.P. 1,706,396, Mar. 26, 1929) describes a cracking process

"Comprising heating, said higher boiling hydrocarbons in a series of tubular heaters wherein heat is supplied to bring said higher boiling hydrocarbons to an active cracking temperature in a primary heating element, then subjecting said higher boiling hydrocarbons to a prolonged heat treatment in a secondary tubular heating element wherein the temperature attained in the primary heating element is maintained by supplying to the hydrocarbons heat sufficient to compensate for the heat rendered latent by the endothermic reaction of decomposition and also for the heat lost by radiation whereby the maximum rate of decomposition for the temperature employed is obtained, then admixing the heated hydrocarbons with an additional supply of hydrocarbons at a relatively lower temperature, then subjecting the admixed hydrocarbons to a final heat treatment whereby the mixture of hydrocarbons is subjected to an active decomposition temperature, and maintaining on the hydrocarbons a pressure sufficient to prevent material vaporisation thereof."

J. C. BLACK (U.S.P. 1,715,980, June 4, 1929) has devised

"A process of cracking crude oil residuum for the production of a relatively small amount of low boiling hydrocarbons, a relatively larger amount of higher boiling hydrocarbons, and a residuum suitable for fuel oil, which comprises, passing a crude oil residuum through a series of cracking coils, under super-atmospheric pressure and at a temperature sufficient to lightly crack the same, and preventing further destructive decomposition of the hydrocarbons of said crude oil residuum by the introduction of a cooler hydrocarbon oil into the final passes of the last cracking coil, in quantities sufficient to maintain the said crude oil residuum below the temperature of excessive cracking and carbonisation."

J. C. BLACK (U.S.P. 1,720,070, July 9, 1929) patents

"A process of cracking oil which comprises heating oil in a confined stream under superatmospheric pressure to crack said oil, measuring the temperature of said oil by pyrometers at a plurality of places along said stream, and injecting oil at points in said stream where fluctuations in temperature, as indicated by said pyrometers, are observed."

"Pressures are in the neighbourhood of 1000 lb. and the temperature between approximately 800° F. and 900° F."

D. G. BRANDT (U.S.P. 1,681,321, Aug. 21, 1928) has devised

"A process of cracking high boiling-point hydrocarbons to form low boiling-point hydrocarbons comprising maintaining a body of high boiling-point oil under pressure, vaporising a lower boiling-point oil in contact with vapours, said lower boiling-point oil having a relatively narrow boiling-point range and said vapours being of the type that remain uncondensed after passing through the ordinary gasoline condenser, passing the mixed vapours through the body of high boiling-point oil to crack the oil, condensing undesired fractions from vapours leaving the high boiling-point oil and mixing this condensate with similar boiling-point oil to form said lower boiling-point oil for the process."

E. M. CLARK and F. A. HOWARD (U.S.P. 1,710,404, Apr. 23, 1929) present

"The process of pressure oil distillation which consists in maintaining in a distilling system a body of oil under pressure and at a temperature suitable for effecting distillation thereof, passing the evolved vapours through a body of oil, thereby heating the oil and condensing a part of the vapours, refluxing the heated oil and condensate from the second body of oil, flowing a stream of oil in indirect heat conductive contact with said second body of oil, thereby heating the stream and cooling the body of oil, and feeding the heated oil from the stream into the second body of oil."

M. W. COLONY (U.S.P. 1,715,341, May 28, 1929) claims a

"Process of treating petroleum oils to convert them into compounds suitable as motor fuels, the steps which consist in maintaining a quantity of petroleum compounds undergoing treatment in a closed reaction chamber, heating up a mass of inert, refractory, heat absorbing material until said material is above the temperature required for the conversion reaction, passing a carrier gas including steam thereover, and thence into said reaction chamber, controlling the temperature of the said reacting compounds whereby the conversion of said petroleum compounds is brought about under substantially uniform temperature conditions, the products from said chamber containing the vapours of the desired compounds of the process in addition to the carrier gas, and subjecting the products from said chamber to conditions producing liquefaction of said compounds suitable as motor fuels."

W. M. CROSS (U.S.P. 1,667,883, May 1, 1928) originates

"A process for treating hydrocarbon oil consisting in fractionally distilling the oil, condensing and separately collecting the respective fractions, withdrawing the tarry residual products, subjecting the gasoline-like fractions to a refining action and redistillation to produce refined gasoline, directing the more refractory fractions and selected portions of the residual material to a cracking stage and there subjecting said fractions and residual material to a conversion temperature and pressures in excess of 500 pounds whereby the conversion is effected substantially in the liquid phase, drawing off the synthetic product, containing a substantial percentage of low boiling oils and cooling it, returning said product to be recycled through the fractional distillation stage and diverting a portion of the heavy residual oils from the system."

"The charging stock to the cracking still is subjected to conversion temperatures in the furnace 17 ranging from 600° to 1,000° F., and pressures in excess of 500 pounds."

W. M. CROSS (U.S.P. 1,696,030, Dec. 18, 1928) patents

"A process for treating petroleum oil consisting in raising the oil to a conversion temperature in a heating stage, passing the oil to a reacting stage and maintaining a pressure from 400 to 750 pounds per square inch upon the heating and reacting stages, introducing a combustion supporting gas to the reacting stage to raise the temperature therein in excess of the temperature in the heating stage, passing the converted product from the reacting stage to a distillation stage maintained under reduced pressure, refluxing the evolved vapours in separate stages of dephlegmation and collecting the separated products."

W. M. Cross (U.S.P. 1,717,007, June 11, 1929) has devised

"A process for converting hydrocarbon oils consisting in heating the oil to a cracking temperature in a heating stage, passing the oil to a reacting stage and there collecting it in a substantial body, maintaining a pressure upon the heating and reacting stages sufficient to prevent any substantial distillation, adding a combustion supporting gas to the reaction stage to supply and maintain temperatures therein in excess of the temperatures in the heating zone, drawing off and cooling the converted product from the reacting stage."

A. D. David (U.S.P. 1,688,855, Oct. 23, 1928) offers

"A process for treating hydrocarbon oil consisting in raising the oil to a cracking temperature while advancing in a stream through a heating zone, in transferring the highly heated oil to an enlarged reaction chamber wherein a substantial body of oil accumulates and wherein no rise in oil temperature occurs, in taking off vapours from said enlarged chamber for condensation and collection, in continuously withdrawing residual oil from said enlarged chamber without recirculating any portion thereof through said heating zone, in maintaining a swirling motion of the liquid oil in said enlarged chamber to hold the carbon in suspension in the oil by withdrawing a portion of the liquid oil therefrom and returning it under an increased pressure to said chamber tangential to the wall thereof."

A. D. David (U.S.P. 1,733,651, Oct. 29, 1929) presents

"An apparatus for treating oil, comprising heating tubes, vaporising, dephlegmating and condensing means, serially connected, means for returning reflux condensate separated out in the dephlegmating means, the means for recycling the reflux condensate for retreatment, comprising casings surrounding the heating tubes forming an annular space between said tubes and casings, through which the reflux condensate passes, means for combining the heated raw oil and the reflux condensate in said vaporising means and means for maintaining a regulated pressure upon the apparatus."

M. F. De Bajligethy (U.S.P. Reissue 17,233, Mar. 12, 1929) arranges

"A still including an outer shell, an inlet line entering the shell, an enlarged reaction drum, within the shell into which said line is connected, a heating coil outside of the shell connected with said inlet line, a housing enclosing the turns of said coil and spaced therefrom forming a fluid circulating chamber about the turns of the heating coil, means for circulating a fluid through said chamber, said circulating means including an outlet line leading from said chamber, and a trap associated with the outlet line."

J. F. Donnelly (U.S.P. 1,712,789, May 14, 1929) outlines

"A process for the conversion of hydrocarbon oils, which consists in heating a mass of relatively heavy hydrocarbon oil to a cracking temperature under a pressure sufficient to prevent vaporisation thereof, discharging said heated oil before the cracking reaction reaches the condition where free carbon would be formed therein into a zone of lower pressure, and checking the cracking reaction in said zone of lower pressure before it reaches the condition where free carbon would be formed therein, in such a degree as to prevent the formation of free carbon in said zone by the simultaneous regulated introduction of a cooler hydrocarbon oil into said zone."

J. F. DONNELLY (U.S.P. 1,714,855, May 28, 1929) patents

"The combination of a combustion chamber, means for generating heat by combustion therein, said chamber having a top provided with passages therethrough, a plurality of pairs of separated walls extending upwardly from said top of said chamber forming passages between said pairs which passages connect with said passages through said top so as to allow the gases of combustion to pass therethrough, said separated walls of each pair being spaced from each other so as to form a passage therebetween adapted to allow a flow of heat-absorbing fluid therethrough, and a passage at the top of each pair of walls adapted to conduct said heat-absorbing fluid into said gases of combustion."

C. P. DUBBS (U.S.P. 1,670,103, May 15, 1928) covers

"A process for cracking oil consisting in passing the oil through a heating coil, thence to a plurality of enlarged chambers connected in series and allowing vaporisation to take place in said chambers and withdrawing the vapours therefrom, withdrawing the liquid residue from each of said chambers independently and diverting predetermined quantities of said residue from predetermined chambers back to the charging stock and commingling the same with said charging stock and sending said mixture through the heating coil to be cracked and maintaining a superatmospheric pressure on the oil during treatment."

C. P. DUBBS (U.S.P. 1,670,104, May 15, 1928) presents for cracking oil

"The combination with a battery of stills, of a reflux condenser comprising a pair of main headers, aerial pipes interposed therebetween, connections between one header and the vapour space of each still, connections between the other header and a final condenser, means for cutting out of the system one or more aerial pipes, pressure regulating valves interposed between the stills and the header connected to the vapour space of said stills, means for drawing off reflux condensate from one of said headers, and means for returning said reflux condensate to any of said stills."

C. P. DUBBS (U.S.P. 1,686,654, Oct. 9, 1928) has originated

"A process for the conversion of hydrocarbon oils, which consists in heating a mass of relatively heavy hydrocarbon oil to a cracking temperature above the boiling point of the complex chemical constituents of said heavy oil under sufficient pressure to prevent vaporisation of said chemical constituents; introducing said heated oil into a zone of lower pressure in such a manner as would permit vaporisation of said chemical constituents and checking the dissociation of said heated oil by the regulated introduction of a cooler mass of hydrocarbon oil into physical contact therewith substantially at the point of vaporisation."

C. P. DUBBS (U.S.P. 1,690,997, Nov. 6, 1928) covers

"In an apparatus for cracking oil, a furnace having heating flues therein, substantially straight vertical heating pipes extending through said heating flues, a supply tank, a connection between said heating pipes and tank, a liquid forcing means and connections from said tank and heating pipes to said means."

C. P. DUBBS (U.S.P. 1,703,100, Feb. 26, 1929) devises

"A process for converting hydrocarbon oil, consisting in subjecting the oil to cracking conditions of temperature and pressure in a heating zone, in passing the evolved vapours to a dephlegmating zone, in dephlegmating the vapours by introducing into the dephlegmating zone in physical contact with the vapours a refractory distillate which will substantially completely vaporise but will not undergo any substantial cracking reaction at the temperature maintained in the dephlegmating zone, to flow through a substantial portion of the dephlegmating zone, in augmenting the dephlegmation of the vapours by passing a less refractory oil in a closed conduit through the dephlegmating zone, and in charging such less refractory oil to said heating zone."

C. P. DUBBS (U.S.P. 1,716,306, June 4, 1929) develops

"A process for cracking hydrocarbon oil under the pressure of self generated vapours which consists in maintaining successive bodies of oil under successively higher temperatures in separated zones, in taking off vapours from each zone and separately subjecting them to reflux condensation, in passing the reflux condensate obtained from the vapours taken off from a zone of lower temperature to the zone of next succeeding higher temperature without permitting such condensate to return to the zone in which the vapours from which it was condensed were generated."

C. P. DUBBS (U.S.P. 1,729,307, Sept. 24, 1929) covers

"A process for converting heavy hydrocarbon oils into lighter hydrocarbon oils comprising advancing a stream of heavy hydrocarbon oil under an applied pressure through a heating coil disposed within a furnace, raising the oil during its passage through said heating coil to a cracking temperature in excess of 800° F. while maintained under superatmospheric pressure sufficient to prevent material destructive distillation of the oil in the heating coil, delivering the highly heated oil from said coil to an enlarged zone, releasing superatmospheric pressure from the oil delivered to said enlarged zone, thus effecting destructive distillation of the oil and substantially a complete separation of the oil into vapours and a relatively dry coke-like residue, removing the vaporous constituents from said enlarged zone, subjecting the vaporous constituents to reflux condensing action to remove therefrom all insufficiently converted materials, continuously supplying a stream of such insufficiently converted materials while in a heated condition under a mechanically imposed pressure to the stream of oil advancing through said heating coil."

E. C. D'YARMETT (U.S.P. 1,732,805, Oct. 22, 1929) claims

"The method of heat treating hydrocarbon oil, including admitting a stream of oil to a confining vessel, circular in cross-section and of extending surface area, rotating the oil at a speed sufficient to maintain the oil in the form of a continuous film on the inner surface of the vessel, heating the vessel, transferring heat from the vessel to the film of oil and collecting vapours evolved from the oil within the space surrounded by said film."

Residue from the vaporisation may be raised to a temperature of 1100° F., and provision is made for

"The introduction of a gas rich in hydrogen, such as methane having a molecular construction denoted by the formula CH_4, into the vapour space surrounded by the film of oil within the heating chamber, where it may be bombarded by molecules freshly formed by cracking the oil, to promote combination of light and heavy molecules of the gas and oil."

GUSTAV EGLOFF (U.S.P. 1,670,106, May 15, 1928) cracks hydrocarbon in an apparatus

"Comprising an enlarged chamber in which a bulk supply of oil is adapted to be maintained and wherein vaporisation occurs, a reflux apparatus located in the vapour space of said enlarged chamber, said reflux apparatus comprising an elongated annular conduit of restricted cross-sectional area, means for passing cool oil though said reflux apparatus to cool the vapours evolved from the oil in said chamber and effect a reflux condensation thereof, means for delivering oil which has passed through said reflux apparatus into the body of oil in said enlarged chamber and means for removing unvaporised oil from said enlarged chamber."

GUSTAV EGLOFF (U.S.P. 1,670,107, May 15, 1928) dehydrates and cracks emulsified oil by

"Distilling the oil under regulated temperatures, and superatmospheric pressure, and simultaneously injecting into the oil in the still, in the vapour space thereof, caustic soda for the purpose of dehydrating the oil."

GUSTAV EGLOFF (U.S.P. 1,670,108, May 15, 1928) covers as defined in two typical claims

"A process for cracking petroleum oil consisting in passing the oil through a heating coil, where it is subjected to cracking conditions of temperature, thence to an expansion chamber removing vapours from said expansion chamber and subjecting them to a reflux condensing action withdrawing residuum from said expansion chamber and recirculating the residuum directly back through said expansion chamber where it is further distilled by returning the same to the vapour space of said expansion chamber, and returning the reflux condensate to said expansion chamber for further treatment."

"A continuous process of oil conversion, consisting in subjecting an advancing stream of oil to a cracking temperature in a heating zone, in passing heated oil from said stream into an enlarged reaction chamber wherein a body of liquid oil accumulates and substantial vaporisation occurs, in dephlegmating the evolved vapours, in continuously withdrawing unvaporised residual oil from said reaction zone, in isolating predetermined portions of such residual oil from the system, in returning the remaining portion of the residual oil under a mechanical pressure directly and without passing the same through said heating zone to the vapour space of said reaction zone for further treatment, and in maintaining a super-atmospheric vapour pressure on the oil in said stream and reaction zone."

GUSTAV EGLOFF (U.S.P. 1,679,208, July 31, 1928) has

"A continuous process of oil conversion comprising advancing a stream of oil through a heating zone wherein it is raised to a cracking temperature, introducing highly heated oil into an enlarged reaction zone wherein

a body of oil accumulates and substantial vaporisation takes place, dephlegmating the evolved vapours, continuously withdrawing unvaporised residual oil from said reaction zone below the liquid level of the oil therein, introducing to the unvaporised residual oil a portion of the uncondensable gases produced in the process, returning such withdrawn residual oil together with the uncondensable gases introduced thereto under pressure directly and without passage through said heating zone into the vapour space of said reaction zone to undergo further treatment therein, and maintaining a super-atmospheric vapour pressure on the oil in said stream and in said reaction zone."

GUSTAV EGLOFF (U.S.P. 1,682,742, Sept. 4, 1928) devises

"A process of cracking oil, consisting in passing the oil through a coil of restricted cross-sectional area, disposed within a furnace wherein the oil is subjected to cracking conditions of temperature and pressure, and in introducing said oil while at a cracking temperature to an enlarged expansion chamber wherein vaporisation occurs, in mechanically agitating the vapours in said chamber by rotating elements disposed therein, and in then passing the vapours from the expansion chamber for dephlegmation, condensation, and collection."

GUSTAV EGLOFF (U.S.P. 1,682,744, Sept. 4, 1928) outlines

"A process of treating hydrocarbon oil, consisting in heating the oil to a conversion temperature, in maintaining the oil in a shallow body in a conversion stage, in recycling the unvaporised portions from said shallow body for re-treatment under higher temperature conditions than the initial treatment, in passing the re-cycled heated oil to said conversion stage and in maintaining it in a separate body therein, in dephlegmating the vapours issuing from both of said oil bodies, in condensing the resulting vapours and in collecting the resulting distillate."

GUSTAV EGLOFF (U.S.P. 1,688,860, Oct. 23, 1928) covers

"A process for cracking hydrocarbon oil consisting in raising the oil to a cracking temperature under a substantial pressure in an initial stage of conversion, dephlegmating and condensing the generated vapours from said stage, passing the unvaporised oil to a top fired secondary zone, and there subjecting it to increased pressure and temperature conditions, dephlegmating and condensing the generated vapours relieved from the secondary zone of reaction and collecting them separately from those produced in the initial stage."

GUSTAV EGLOFF (U.S.P. 1,703,617, Feb. 26, 1929) presents

"A process of treating hydrocarbon oils, consisting in heating the oil in a plurality of independent units, in dephlegmating the evolved vapours, in continuously returning the reflux condensate to each heating unit for re-treatment, in condensing the vapours resulting from such dephlegmation and in collecting the resulting distillate, in passing the uncondensed gases produced in each unit to a common header while preventing the return of incondensable gases from said header into any one of said units, compressing the incondensable gases collected in said header, and in returning said compressed gases in regulated quantities to the raw oil treated in each unit."

GUSTAV EGLOFF (U.S.P. 1,705,181, Mar. 12, 1929) proposes

"A process for converting hydrocarbon oils, which comprises heating a stream of heavy hydrocarbon oil to a relatively mild cracking temperature, introducing such heated heavy hydrocarbon oil into an enlarged reaction zone, separately heating a stream of relatively light hydrocarbon oil to a severe cracking temperature, to raise said light oil above the cracking temperature of said heavy hydrocarbon oil, introducing the highly-heated light hydrocarbon oil to said reaction zone, to substantially completely vaporise therein and augment the cracking of the heavy hydrocarbon oil in said reaction zone, subjecting vapours issuing from said reaction zone to reflux condensation, forming reflux condensate, subjecting the reflux condensate so formed to independent heat treatment, and thence returning the same to said reaction zone."

GUSTAV EGLOFF (U.S.P. 1,707,348, Apr. 2, 1929) claims

"A continuous process for cracking hydrocarbon oil, consisting in introducing charging oil in intimate contact with evolved vapours flowing through a dephlegmator, in taking off dephlegmated vapours from the dephlegmator for condensation and collection, in passing the charging oil, together with reflux condensate separated from the vapours, from said dephlegmator to an enlarged vaporising zone, counter-current to the flow of the vapours from such enlarged zone to the dephlegmator, in maintaining the preheated charging oil and reflux condensate in a pool in said enlarged vaporising zone, in passing preheated charging oil and reflux condensate from said pool through a heating zone wherein such substances are heated to a cracking temperature, in introducing these highly-heated substances from the heating zone to an independent pool in said enlarged vaporising zone from which independent pool heavy unvaporised residual oil is continuously withdrawn to be isolated from the system and from which no oil is returned to the heating zone, and in maintaining a super-atmospheric pressure on the oil undergoing conversion."

GUSTAV EGLOFF (U.S.P. 1,707,349, Apr. 2, 1929) presents

"In an apparatus for converting petroleum oil, the combination with means for heating the oil to a conversion temperature, of an expansion chamber comprising inner and outer receptacles wherein the oil is maintained in conversion pools, means for directing the oil from the heating means to the inner receptacle to overflow into the outer receptacle, dephlegmating and condensing means, means for returning the reflux condensate from the dephlegmating means to the expansion chamber for re-treatment, and independent means for withdrawing the unvaporised products from the separate receptacles while maintaining a regulated pressure upon the oil undergoing treatment.

GUSTAV EGLOFF (U.S.P. 1,710,152, Apr. 23, 1929) claims

"A process of converting relatively high boiling point hydrocarbons into those of lower boiling point, consisting in heating the oil in the still under vapour pressure, taking off vapours therefrom, passing such vapours in relatively small separated streams through the lower portion of the still out of contact with the main body of oil in the still, subjecting the superheated vapours to a reflux condensing action and returning such reflux condensate to the body of oil in the still."

GUSTAV EGLOFF (U.S.P. 1,710,153, Apr. 23, 1929) has invented

"A process of treating hydrocarbon oil, consisting in charging the lower of a pair of superimposed stills with a bulk supply of oil, in passing the heating gases through a closed conduit located within said still, in passing the vapours generated in said lower still to the upper still, wherein they are superheated by passing the combustion gases through a closed conduit located in said upper still, in continuously introducing a spray of preheated oil into said bulk supply of oil, in dephlegmating the vapours passing over from said upper still, in returning the reflux condensate resulting from such dephlegmation to said bulk supply of oil, in continuously withdrawing heavy residuum from said bulk supply of oil, and in maintaining a superatmospheric vapour pressure on the oil undergoing conversion."

GUSTAV EGLOFF (U.S.P. 1,722,043, July 23, 1929) covers

"A process for treating hydrocarbon oil, consisting in subjecting a body of oil to cracking conditions of heat and pressure in a still, in subjecting the evolved vapours to dephlegmation, in withdrawing regulated quantities of the unvaporised oil from the body of oil in the still, in combining such unvaporised oil with reflux condensate resulting from the dephlegmation of the vapours, in passing the resulting mixed oil through a mass of heated filtering material, in returning the cleansed mixed oil, and injecting it into the lower portion of the oil body undergoing cracking reaction."

GUSTAV EGLOFF (U.S.P. 1,733,654, Oct. 29, 1929) claims

"The process of converting heavy into lighter hydrocarbons, comprising passing oil through a cracking coil in a heated condition to a vapour chamber so positioned as to incline from the horizontal and disposed adjacent said cracking coil, in discharging vapours from the lower end of said inclined chamber to a dephlegmator, in returning reflux condensate from the dephlegmator directly to the lower end of the inclined chamber, in discharging said condensate and light residue from the lower end of said chamber for repassage through the heating coil, in discharging heavy residuum from substantially the bottom of said lower end of the inclined chamber without returning said residuum to the cracking coil, and in maintaining a super-atmospheric pressure on said system."

GUSTAV EGLOFF and H. P. BENNER (U.S.P. 1,670,105, May 15, 1928) arrange

"In an apparatus for cracking petroleum oil, the combination with a furnace, of means for heating the furnace to a cracking temperature, of a first pair of horizontal stills mounted in the lower part of the furnace, a second pair of horizontal stills mounted in the furnace and superimposed above said first pair, a single horizontal still in said furnace superimposed above and positioned between the stills of said second pair, means for delivering oil to said first pair of stills to substantially fill the same without filling the other stills, means connecting the first pair of stills with the superimposed stills whereby vapours from said first pair pass through and are superheated in said superimposed stills, a dephlegmator, connections from the single still to said dephlegmator, means for discharging uncondensed vapours from the dephlegmator, and means for returning reflux condensate from said dephlegmator to one of said first pair of stills."

GUSTAV EGLOFF and HARRY P. BENNER (U.S.P. 1,703,103, Feb. 26, 1929) claim

"A process of treating emulsified hydrocarbon oil, consisting in heating the oil to a conversion temperature, in passing evolved vapours to a dephlegmator, in subjecting the reflux condensate to further treatment at a temperature above the boiling point of water, in subjecting the dephlegmated vapours to an initial condensing action at a temperature above the boiling point of water, in uniting the water vapours and light hydrocarbon vapours, separated from the reflux condensate and from the vapours undergoing such initial condensation and in thereafter subjecting such commingled water vapours and light hydrocarbon vapours to a final condensing action."

GUSTAV EGLOFF and H. P. BENNER (U.S.P. 1,725,067, Aug. 20, 1929) have devised

"A method for cooling the heating coil of a coil and chamber oil cracking apparatus of the character in which oil is continuously supplied to the heating coil, raised to a cracking temperature therein, and thence delivered to the chamber and which includes pipe connections for cyclically circulating oil from the bulk supply, comprising discontinuing the application of heat to the heating coil, ceasing the delivery of oil from the coil to the chamber, continuing the passage of cool oil through the coil, returning the oil subsequent to its passage through the coil to a bulk supply of cool oil, from which supply oil is being delivered to the coil until the coil is sufficiently cooled."

GUSTAV EGLOFF and H. P. BENNER (U.S.P. 1,729,035, Sept. 24, 1929) have designed for pressure distillation

"A vapour expansion chamber consisting of a relatively stationary outer shell and a removable inner shell concentric with said outer shell, said inner shell being open at both ends and formed of a plurality of separable segments."

GUSTAV EGLOFF and HARRY P. BENNER (U.S.P. 1,733,655, Oct. 29, 1929) arrange

"In an apparatus for treating oil, the combination with a pair of superimposed longitudinally extending still members, means for heating the upper portion of the lower still member so as to produce surface distillation of the contents thereof, means for superheating the vapours in the upper still member, and means for rotating said still members."

"For example, if the process is carried out at atmospheric pressure the oil in the lower still member might be subjected to surface distillation at a temperature of from 450° F. to 750° F., while the vapours in the upper still member might be heated at a temperature of 800° F. to 1200° F."

CARLETON ELLIS (U.S.P. 1,716,433, June 11, 1929) presents

"The process of cracking heavy oil which comprises forcing an ignited fuel mixture comprising liquid fuel and air beneath the surface of a body of oil under pressure; whereby the latter is heated to a cracking temperature."

In some cases the operation is carried out at atmospheric pressure or 4 to 20 atmospheres or more may be employed.

FRANK B. FRETTER (U.S.P. 1,707,606, Apr. 2, 1929) covers the

"Method of treating fluid hydrocarbons, which consists of rapidly impelling the treated hydrocarbon through a heater under extraneous pressure approximating 1,000 pounds per square inch and obtaining a working temperature for said hydrocarbon in excess of 800° F., permitting the escape from the heater of graduated volumes of the hydrocarbon through an accelerating vent having the characteristics of the Venturi tube into a vaporising chamber at approximately atmospheric pressure, and separating the heavier and lighter hydrocarbons resulting from this treatment, substantially as set forth."

L. J. GARY (U.S.P. 1,676,895, July 10, 1928) describes

"An apparatus for cracking hydrocarbon oil, comprising a plurality of independent heating coils, a plurality of expansion chambers, into which heated oil from said coils is discharged, a dephlegmator associated with each of said enlarged expansion chambers, pressure reducing means interposed between each enlarged expansion chamber and its associate dephlegmator, a common header in communication with the vapour space of each of said expansion chambers, a second header in communication with each of said dephlegmators, whereby a uniform pressure can be maintained in said dephlegmators, lower than a uniform superatmospheric pressure maintained in said enlarged expansion chambers, and means connected to said dephlegmators for condensing and collecting vapours issuing therefrom."

G. W. GRAY (U.S.P. 1,724,760, Aug. 13, 1929) covers as described in two claims

"The process of converting heavy hydrocarbon oils into oils of lower boiling point which comprises subjecting oil to a cracking temperature and pressure in a pressure zone, separating the high boiling fractions of the evolved vapours from the low boiling fractions in the form of a condensate, then subjecting the condensate while still hot to increased cracking temperature and pressure, simultaneously distilling another independent body of oil, separating the evolved vapours according to their boiling points, and commingling the condensate thus formed with the oil in one of the pressure zones,"

and

"the process of converting heavy hydrocarbon oils into oils of lower boiling point which comprises, subjecting oil to a cracking temperature and pressure in a pressure zone, separating the high boiling fractions of the evolved vapours from the lower boiling fractions in the form of a condensate, subjecting the condensate while still hot to increased cracking temperature and pressure, simultaneously distilling another independent body of oil, passing the evolved vapours through a plurality of fractionating devices to separate them according to their boiling points, and commingling the condensates thus formed in each of the fractionating devices with the oil in one of the pressure zones."

W. S. HADAWAY, JR. (U.S.P. 1,678,728, July 31, 1928), has invented

"Apparatus for converting higher boiling hydrocarbons into lower boiling ones comprising a vertical cracking chamber, a multi-tubular exchanger disposed longitudinally within the cracking chamber and formed with outlets at the upper end thereof, means for introducing oil into the bottom of the exchanger, mechanical means for agitating the contents of the cracking chamber and means for drawing off liquid from the bottom of the cracking chamber."

R. W. HANNA (U.S.P. 1,724,476, Aug. 13, 1929) has developed

"A process of cracking mineral oils which comprises heating the oil under pressure to a temperature sufficient to form vapours from such oil, then separating the oil into vapours and liquid, separately raising the pressure on said vapours and liquid and recombining the same whereby the oil is materially raised in temperature by the heat of the compression of the vapours and brought to a pyrogenetic decomposition temperature, passing the oils into a reaction zone, and therein maintaining a comparatively small volume of liquid to vapour."

E. C. HERTHEL (U.S.P. 1,677,774, July 17, 1928) claims

"In processes of cracking higher boiling hydrocarbon oils to produce lower boiling hydrocarbon oils by distillation under pressure at cracking temperatures in which unvaporised oil is withdrawn from the pressure distillation during operation and subjected to further vaporisation by its self-contained heat through reduction in pressure."

E. C. HERTHEL (U.S.P. 1,683,184, Sept. 4, 1928) provides

"In a pressure still comprising a bulk supply drum in which a bed of filtering or absorbent material is arranged extending entirely across the drum and below the normal liquid level therein, a battery of heating tubes and connections for circulating oil from the space in the bulk supply drum beneath the bed of filtering or absorbent material through the battery of heating tubes and back to the space in the bulk supply drum above the bed of filtering or absorbent material, venting means connecting the upper part of the space beneath the bed of filtering or absorbent material and the space in the upper part of the bulk supply drum above the normal liquid level therein."

"The pressure in the system may, for example, be maintained in the neighbourhood of from 100 to 150 pounds per square inch."

E. C. HERTHEL (U. S. P. 1,721,779, July 23, 1929) covers in cracking

"The improvement which comprises bringing an initial charge of oil to cracking conditions of temperature and pressure, then taking off vapours of the cracked oil from the vaporising zone while circulating and recirculating higher boiling oil through the heating zone from and to the vaporising zone and supplying raw oil to the oil circulating through the heating zone until a substantial amount of cracked oil has been taken off, and then, before the oil circulating through the heating zone becomes saturated with pitch, stopping the recirculation of unvaporised oil from the vaporising zone through the heating zone while continuing to take off vapours of the cracked oil from the vaporising zone and to circulate raw oil through the heating zone until a further substantial amount of cracked oil has been taken off."

E. C. HERTHEL (U.S.P. 1,721,780, July 23, 1929) arranges

"A pressure still system comprising a vaporising drum and a battery of heating tubes, a connection opening upwardly into the vaporising drum below the normal liquid level therein for circulating oil from the vaporising drum to the heating tubes, a forcing means in said connection, a connection for circulating oil from the heating tubes to the vaporising drum, a reflux tower and vapour connection between the same and the vapour space of the vaporising drum, a valve arranged at the upper end of said first mentioned connection and an operating extension therefor extending upwardly through the vaporising drum and through the

vapour space within the same and passing through the wall of the vaporising drum above the normal liquid level therein, and a reflux return connection from the reflux tower opening into said first mentioned connection between said valve and said forcing means."

E. C. HERTHEL AND H. L. PELZER (U.S.P. 1,703,528, Feb. 26, 1929) present

"In the cracking of hydrocarbon oils by distillation under pressure in pressure still systems in which the charge of oil is circulated from a bulk supply tank through an externally heated tubular heater and back to the bulk supply tank, the improvement comprising maintaining a bed of material containing uncombined metallic oxides in the bulk supply tank submerged, indirectly exposed to and extending entirely across the charge of oil therein and supported upon a support adapted to retain said material but to permit free passage of the still charge, supplying oil to the heating tubes from below said bed of material, and discharging the oil from the heating tubes directly into the charge of oil in the bulk supply tank above the support and material thereon."

"For example, with a gas oil charging stock, a pressure in the neighbourhood of 90 to 100 lb. or up to 125 lb. or more can be used. With a lighter kerosine charging stock, a higher pressure, for example, from 125 lb. up to 300 lb. or more is used with advantage."

E. C. HERTHEL AND H. L. PELZER (U.S.P. 1,703,529, Feb. 26, 1929) claim

"The improvement in the cracking of hydrocarbon oils by distilling a charge of the oil under pressure at a cracking temperature in a circulatory pressure still in which the oil is heated to a cracking temperature in a tubular heater, which comprises maintaining in said still charge a body of fuller's earth on a support adapted to permit free passage of oil and extending entirely across the charge of oil in the pressure still, withdrawing oil from beneath said support and discharging the oil directly into the charge of oil above said support and the material supported thereon, and continuing the operation until the pitch content of the still charge builds up at least to saturation."

E. C. HERTHEL AND H. L. PELZER (U.S.P. 1,714,090, May 21, 1929) present

"An improved method of cracking hydrocarbon oils, which comprises maintaining a body of oil at a cracking temperature and taking off vapours including vapours of the cracked product therefrom under pressure, circulating oil from the body through heating tubes externally exposed to heating gases and back to the body, maintaining a bed of finely divided filtering material in the body of oil in the path of the circulating oil, and introducing a gaseous heating medium heated to a cracking temperature into the body of oil beneath the bed of finely divided filtering material."

E. C. HERTHEL AND H. L. PELZER (U.S.P. 1,733,799, Oct. 29, 1929) claim

"An improved method of cracking hydrocarbon oils by distillation under pressure, which comprises circulating a charge of oil in a pressure still from a bulk supply drum through heating tubes and back to the bulk supply drum and heating it to a cracking temperature in the heating tubes, taking off vapours including vapours of the cracked product from the bulk supply drum under pressure, maintaining within the charge of oil in the bulk supply drum below the normal liquid level therein and directly exposed to the oil therein a body of fuller's earth, said body of fuller's earth being arranged to permit free circulation of oil and to provide open liquid paths through the bulk supply drum from and to the

heating tubes, circulating oil supplied from the heating tubes to the bulk supply drum in part directly through said body of fuller's earth and back to the heating tubes and in part through said open liquid paths and back to the heating tubes, and supplying raw oil to and discharging pitch-laden oil from the charge of oil in the pressure still during the distillation."

"For the production of gasoline or a gasoline-containing pressure distillate from gas oil, for example, pressures up to 125lb. per square inch or higher pressures may be used."

E. C. HERTHEL AND H. L. PELZER (U.S.P. 1,714,091, May 21, 1929) devise

"An improved method of cracking hydrocarbon oils, which comprises circulating a charge of oil in a pressure still from a bulk supply drum through heating tubes back to the bulk supply drum and maintaining a body of finely divided absorbent material in the bulk supply drum above supporting means adapted to retain the finely divided absorbent material but to permit free passage of oil and extending entirely across the path of the circulating still charge, heating the oil to a cracking temperature in the heating tubes, taking off vapours including vapours of the desired product under pressure, and agitating the body of finely divided absorbent material in the bulk supply drum."

E. C. HERTHEL AND T. DE C. TIFFT (U.S.P. 1,677,772, July 17, 1928) outline

"An improved method of producing lower boiling hydrocarbon oils from higher boiling hydrocarbon oils, which comprises forcing such higher boiling hydrocarbon oils in a single pass through a heating zone into a primary vaporising zone and maintaining the oil under superatmospheric pressure in both the said heating zone and the primary vaporising zone, passing unvaporised oil from the primary vaporising zone to an externally unheated secondary vaporising zone and maintaining the oil therein under a pressure lower than that prevailing in the primary vaporising zone, taking off and condensing vapours from the secondary vaporising zone and forcing oil condensed from these vapours again through the heating zone, first in advance of fresh oil and then in admixture with fresh oil, without returning to the heating zone unvaporised components of oil which have once passed therethrough, passing heating gases in the heating zone first in heat exchange with the oil condensed from vapours from the secondary vaporising zone and then in heat exchange with the mixture of this oil with fresh oil, and taking off vapours from the primary vaporising zone including vapours of the desired lower boiling hydrocarbon oils."

E. C. HERTHEL AND T. DE C. TIFFT (U.S.P. 1,677,773, July 17, 1928) covers in cracking processes

"In which unvaporised oil is withdrawn during the pressure distillation and subjected to further vaporisation by its self-contained heat under a reduced pressure, the improvement which comprises passing the vapours separated from the oil withdrawn from the pressure distillation into a tower, introducing fresh oil directly into the vapour space in this tower, so as to bring the fresh oil and vapours into direct and intimate contact therein, thereby subjecting the vapours to condensation, passing the vapours from the pressure still into a reflux tower and introducing admixed condensate and unvaporised fresh oil from the first mentioned tower into direct contact with the vapours therein, and returning reflux together with admixed unvaporised oil from the said reflux tower to the pressure distillation."

E. C. Herthel and T. De C. Tifft (U.S.P. 1,677,775, July 17, 1928) present

"An improved method of cracking hydrocarbon oils, which comprises maintaining a body of oil in a vaporising zone under a superatmospheric pressure and heating it to a cracking temperature by circulating oil therefrom through heating tubes and back thereto, taking off vapours including vapours of the cracked product therefrom under pressure, discharging oil from the said body into a separate vaporising zone maintained under a pressure lower than that prevailing in the first and taking off vapours from the second vaporising zone, subjecting the vapours from the second vaporising zone to a condensing operation and forcing condensate from this condensing operation through separate heating tubes into the first vaporising zone, and passing heating gases from a firebox in which fuel is burned for supplying heat to the cracking operation first over the heating tubes through which condensate from the said condensing operation is forced and then over the heating tubes through which oil from the said body is circulated."

E. C. Herthel and T. De C. Tifft (U.S.P. 1,677,776, July 17, 1928) describe

"An improved method of cracking hydrocarbon oils which comprises forcing raw oil in a single pass through a heating zone into a vapourising zone and maintaining the oil under superatmospheric pressure in both the heating zone and the vaporising zone, heating the oil to the cracking temperature in the said heating zone, subjecting the vapours from the said vaporising zone to a refluxing operation, passing unvaporised oil from the said vaporising zone to a second vaporising zone and maintaining the oil therein under a pressure lower than that prevailing in the first vaporising zone, subjecting vapours from the second vaporising zone to a separate refluxing operation and forcing reflux condensate therefrom in a single pass through the said heating zone in admixture with raw oil, passing reflux condensate from the said first mentioned refluxing operation in a single pass through a separate heating zone and heating the oil to a cracking temperature therein, maintaining superatmospheric pressure on the second mentioned heating zone at least as high as that maintained on the first mentioned vaporising zone discharging the hot oil products from the second mentioned heating operation directly to the second mentioned vaporising zone and taking off vapours from both refluxing operations."

Pressures of 50 to 200 lb. per square inch or higher are employed.

F. A. Howard and N. E. Loomis (U.S.P. 1,670,037, May 15, 1928) claim in cracking apparatus

"For the conversion of oil, a combination of a coil, means for forcing oil therethrough, means for heating the coil to secure cracking temperature therein, and enlarged chamber into which the coil discharges, said chamber being provided with means for hindering the escape of heat from the chamber, thereby maintaining a cracking temperature therein, a second enlarged chamber into which the first mentioned chamber discharges, and means for supplying heat internally within the second chamber to maintain a cracking temperature therein, which comprises forcing the oil to be converted through a highly heated confined passageway with sufficient velocity to prevent substantial deposition of coke, the oil being thereby brought to conversion temperature, discharging the oil into and through a succession of enlarged chambers, the contained heat of the oil being confined in the earlier of said chambers to maintain the oil therein at conversion temperature and the later of said chambers being heated only sufficiently to maintain the oil at conversion temperature."

F. A. HOWARD (U.S.P. 1,676,826, July 10, 1929) covers

"The method of simultaneously skimming and cracking hydrocarbon residue through a conduit heated to a temperature such that the oil attains a temperature of 750 to 900° F. while travelling therethrough with a velocity such as to prevent substantial deposition of carbon therein, passing the oil into an enlarged drum, holding the liquid oil in said drum at a temperature above 720° F., exerting pressure upon the oil in the conduit and drum to maintain the unchanged charging stock in liquid phase, continuously drawing off the mixed products of conversion from the top of the drum, conveying the products into a chamber in which pressure is released, separately withdrawing the vapours and residues from said chamber, passing crude oil containing low boiling point constituents successively into heat-exchange contact with the vapours from the last mentioned chamber, the residues from said chamber and the converted products issuing from the enlarged drum while passing from the enlarged drum to the chamber in which pressure is released, separately withdrawing the vapours given off from the crude oil and introducing the residue therefrom into the first mentioned heated conduit."

F. A. HOWARD (U.S.P. 1,676,694, July 10, 1928) claims

"The process of pyrogenesis of petroleum products which consists in delivering a stream of products of petroleum, heated to an active cracking temperature, into a primary drum in which the products remain at an elevated temperature, above a cracking temperature, but below the temperature at which they are delivered, removing admixed products of conversion continuously from the primary drum and passing them through a secondary drum of similar form, maintaining in the secondary drum a temperature substantially below that in the primary drum, and recirculating a portion of liquid products from the secondary drum directly into the primary drum."

F. A. HOWARD (U.S.P. 1,681,899, Aug. 21, 1928) has devised

"Apparatus which comprises a furnace, a heating coil in said furnace located as a screen to absorb radiant heat, a distillation chamber into which said coil discharges, another heating coil in said furnace screened by the first-mentioned coil and receiving vapours from the distillation chamber, an enlarged passage-way into which the last-mentioned coil discharges, means for maintaining the temperature in the enlarged passage-way without substantial decline, a vapour line leading from said enlarged passage-way and having a downward slope therefrom, a rectifier for the vapours, a vapour line from the top of said rectifier, a condenser on said vapour line, a tank for receiving condensate, means for returning condensate from said tank into the top of the rectifier, and means for returning reflux from the bottom of the rectifier to the distillation chamber."

F. A. HOWARD (U.S.P. 1,694,262, Dec. 4, 1928) presents

"A process for conversion of hydrocarbons into lower boiling products which comprises feeding a stream of light gas oil into a heating passage-way at a temperature around 900°–1000° F., to effect a material amount of cracking in vaporous condition, then passing the products into a further passage-way which is guarded against heat loss, while also introducing a heavy gas oil, contacting said vapour and liquid products together for a substantial period of time and allowing conversion substantially in the liquid phase, to go on in the mixture solely on the heat

already acquired, and passing the liquid products together with any vapours, from a point substantially above the bottom of the passage-way guarded against heat loss into a vapour-separating zone and separating the lighter hydrocarbons from the heavier."

W. R. HOWARD (U.S.P. 1,674,827, June 26, 1928) covers

"A process of treating petroleum oil consisting in feeding oil to a still by means of a steam pump located in the still, preheating the oil before it enters the steam pump, discharging exhaust steam from the pump into the body of the oil in the still and taking off vapours from the still and condensing and collecting them and maintaining a pressure in excess of 50 lb. to the sq. in. on the oil during distillation."

W. R. HOWARD (U.S.P. 1,715,066, May 28, 1929) has devised

"An apparatus for treating hydrocarbon oil, comprising means for heating an advancing stream of oil to a cracking temperature, an enlarged reaction zone, means for passing heated oil from said stream to a compartment within said enlarged reaction zone, dephlegmating means, means connecting said enlarged reaction zone with said dephlegmating means, means for collecting a body of reflux condensate in a second compartment in said enlarged reaction zone, means for applying heat only to that compartment of the reaction zone containing the reflux condensate, and means for maintaining a superatmospheric pressure on the oil undergoing treatment in the apparatus.

"The process may be operated under a uniform pressure of from 50 to several hundred pounds, the pressure being reduced to atmospheric, subsequent to cracking, by or differential pressures may be used in the cracking process, for example, a pressure of 500 lb. on the heating coil, 300 lb. on the expansion chamber, 200 lb. on the dephlegmator and 100 lb. on the condenser and receiver. The same temperature may be used throughout the cracking process or a higher temperature maintained on the expansion chamber than on the heating coil."

L. C. HUFF (U.S.P. 1,685,488, Sept. 25, 1928) covers

"The step of heating oil in an oil cracking process, which consists in continuously passing the oil in a restricted stream through an elongated conduit disposed within a furnace, wherein the oil is raised to a cracking temperature, in stepping up the velocity of flow of the oil stream through said conduit, and in assisting in the heating of the oil in the stream by introducing a super-heated inert gas into the oil stream in successive sections of said conduit under a pressure in excess of the pressure on the oil stream and at a velocity greater than the velocity of flow of the oil stream."

The inert gas may be superheated steam.

L. C. HUFF (U.S.P. 1,716,136, June 4, 1929) claims

"An apparatus for distilling hydrocarbons under high temperature conditions, comprising a still positioned in a furnace, a plurality of conduits extending along the exterior lower surface of the still, means for supplying steam to said conduits, a plurality of conduits extending along the lower interior surface of the still, means for supplying steam, subsequent to passage through said first conduits, to said second conduits, said second conduits being so perforated that the steam will be directed directly against the lower interior surface of the still, whereby direct

application of extremely hot combustion gases to the lower portion of the still is prevented and coke deposition upon the interior surface of the lower portion of the still avoided.

"A temperature of 800°–1000° F. may be maintained on the liquid in the still. A pressure of from five to several hundred pounds may be maintained on the system, or it may be operated at atmospheric pressure."

E. W. Isom (U.S.P. 1,722,147, July 23, 1929) covers

"An improved process for cracking hydrocarbon oils comprising passing a stream of oil once through a heating conduit and heating it to a cracking temperature therein, discharging the hot products from the heating conduit directly into a body of oil maintained in a reservoir at a cracking temperature, taking off vapours from the reservoir and subjecting them successively to a first and a second refluxing operation, passing fresh relatively refractory oil in indirect heat exchanging relation with the vapours in the first refluxing operation and thereby cooling and refluxing the vapours and preheating the fresh oil, supplying fresh oil, so preheated to the body of oil in the reservoir, passing fresh relatively more refractory oil in indirect heat exchanging relation with the vapours in the second refluxing operation thereby cooling and refluxing the vapours and preheating this fresh oil, and forcing reflux condensate from both refluxing operations together with fresh oil pre heated in the second refluxing operation through said heating conduit."

E. W. Isom (U.S.P. 1,722,222, July 23, 1929) has developed

"An improved process for cracking hydrocarbon oils comprising passing a stream of oil once through a heating conduit and heating it to a cracking temperature therein, discharging the hot products from the heating conduit directly into a body of oil maintained in a reservoir at a cracking temperature, passing an additional supply of fresh oil through a reflux condenser in indirect heat exchanging relation with the vapours generated in the cracking operation to preheat the fresh oil and condense the heavy insufficiently cracked vapours and introducing the fresh oil so preheated directly into the body of oil in the reservoir, subjecting the uncondensed vapours from the first refluxing operation to a further refluxing operation in direct contact with fresh oil, returning the condensate from both refluxing operations together with unvaporised fresh oil from said further refluxing operation to the heating conduit, and drawing off unvaporised residual oil from the reservoir."

E. W. Isom (U.S.P. 1,722,223, July 23, 1929) has devised

"A method of cracking hydrocarbon oils, comprising maintaining a body of oil at a cracking temperature by circulating oil from said body through heating tubes and back to said body and heating the oil to a cracking temperature in said heating tubes, taking off vapours from said body of oil and subjecting them to a refluxing operation, forcing reflux condensate from said refluxing operation once through a separate heating conduit and heating it therein to a cracking temperature, and discharging hot oil products from said heating conduit into the oil circulating from said body of oil to said heating tubes."

Temperatures to 1110° F. may be used, with pressure of 125 lb. per sq. in. or higher.

E. W. Isom and J. E. Bell (U.S.P. 1,676,202, July 3, 1928) devise an apparatus consisting of

"A circulatory oil cracking still having a still proper, heating pipes in a furnace and connections between said still and heating pipes, a circulatory pump arranged to circulate hot oil from said still to and through said heating pipes and back to the still, said pump having loosely fitting bearings and means for forcing relatively cool oil through said bearings into said pump and circulatory system."

E. W. Isom and J. E. Bell (U.S.P. 1,676,203, July 3, 1928) describe

"A method of cracking oil, which comprises circulating the oil from and to a bulk supply tank through a heater maintained at a cracking temperature by and through a circulating pump having a drive shaft in loosely fitting bearings while maintaining the oil under superatmospheric pressure; feeding fresh oil to the still, and forcing a substantial part of this fresh oil through the pump bearings into the hot circulating oil."

E. W. Isom and E. C. Herthel (U.S.P. 1,683,193, Sept. 4, 1928) present

"An improved method of producing gasoline from crude petroleum, which comprises maintaining a body of oil in a vaporising zone and maintaining a bed of finely divided absorbent or filtering material within said body and extending entirely across it, circulating oil from said body from beneath said bed of finely divided material through heating tubes and back to the body of oil above said bed of finely divided material and heating it to a mild cracking temperature therein, supplying crude petroleum to the circulating body of oil, taking off vapours including vapours of the gasoline product from said vaporising zone, and taking off residual oil from the body of oil from beneath said bed of finely divided material."

E. W. Isom, E. C. Herthel and H. L. Pelzer (U.S.P. 1,727,707, Sept. 10, 1929) have devised

"A process of cracking heavy hydrocarbons for the production of lighter hydrocarbons and coke, which comprises heating an externally unheated body of the oil to be cracked to a cracking temperature under pressure and distilling off the cracked hydrocarbons as formed by injecting into said body vapours of hydrocarbons at a temperature above the cracking point, and thereafter injecting superheated steam into the residuum beneath the free surface thereof while discontinuing the injection of hydrocarbon vapours."

E. W. Isom and C. L. Parmelee (U.S.P. 1,675,558, July 3, 1928) disclose

"A process of cracking heavy hydrocarbons to produce lighter hydrocarbons comprising passing the oil through a heating zone of restricted cross section, heating it therein to a cracking temperature and adding to the oil at an intermediate point of said heating zone during its passage therethrough and before the heated oil becomes saturated with tar and oil capable of acting as a solvent for the tar formed during cracking."

E. W. Isom and A. C. Vobach (U.S.P. 1,676,204, July 3, 1928) position

"In tubular oil cracking pressure stills, a bulk supply drum, a battery of heating tubes connected in multiple, and means for circulating heating gases thereover, connections between the bulk supply drum and the

battery of heating tubes including a forcing means, whereby oil may be circulated from and to the bulk supply drum through the battery of heating tubes, in a direction generally countercurrent to the flow of heating gases thereover, the upper ends of the battery of heating tubes being below the usual liquid level in the bulk supply drum, said heating tubes having stationary solid cores formed of twisted rods, arranged in and extending centrally therethrough, leaving a continuous annular oil passage through said heating tubes."

J. J. JAKOSKY (U.S.P. 1,689,590, Oct. 30, 1928) describes

"The process of cracking petroleum or petroleum products which comprises passing the material to be cracked under pressure through a retort, heating such retort to a sufficient temperature to effect cracking thereof, the pressure being such as to maintain the uncracked material substantially wholly in the liquid phase while permitting vaporisation of cracked products, removing vaporised products of such cracking at a plurality of points distributed lengthwise of said retort subjecting each of such vaporised products to a separate electrical precipitating operation to remove liquid particles therefrom and returning the material precipitated from each of such products to the retort at substantially the point at which such product was removed and then collecting such vaporised products."

H. C. KIRK (U.S.P. 1,676,230, July 3, 1928) has described

"A process of heat treating hydrocarbon oils to produce lighter distillates therefrom which comprises injecting oppositely directed non-planar oil streams within a body of oil under conversion conditions of temperature and pressure, to produce circulation within the body of oil of character and velocity sufficient to prevent formation of hard carbon."

A. S. KNOWLES (U.S.P. 1,717,884, June 8, 1929) outlines

"The process of treating heavy hydrocarbon matter in liquid form which comprises depositing the same in divided form on to a thin bed of loose material which is mostly carbon within a closed chamber, while heating said chamber externally from below so as to maintain at least a portion of said bed at a temperature sufficient to cause chemical decomposition of the hydrocarbon matter and deposition of carbon on said loose material, allowing the hydrocarbon matter to pass down a substantial distance into said portion of the bed, and removing the gases and vapours upwardly through the portion of the bed thereabove."

O. D. LUCAS and E. L. LOMAX (U.S.P. 1,690,416, Nov. 6, 1928) crack oils by heating rapidly

"To the cracking temperature in a tube still, passing the heated oils into a conversion chamber in which they are maintained in bulk at the cracking temperature, and at a pressure of from 600 to 1,000 lbs. per square inch, drawing off the lighter oils in vapour form into a vapour pressure or refluxing chamber open directly to and forming an extension of the conversion chamber and consequently at the same pressure of 600 to 1,000 lbs. per square inch, maintaining the said refluxing chamber at a temperature substantially below that of the conversion chamber, but sufficiently high to prevent, under the said pressure common to the conversion and refluxing chambers, the condensation of any oils below a predetermined density, condensing the heavier oils in the aforesaid refluxing chamber and then passing the condensed oils without reheating

and below the cracking temperature through a branch passage directly back into the conversion chamber for further treatment, simultaneously drawing off liquid oils from the conversion chamber, releasing the said liquid oils through a pressure-reducing valve into a lower pressure chamber, and removing the vapour of the lighter oils from the said lower pressure chamber."

A. E. MILLER (U.S.P. 1,714,097, May 21, 1929) offers

"An improvement in the distillation of heavy petroleum distillates and residues for the production of gasoline therefrom, which comprises maintaining a body of the heavy oil at a temperature between about 575°F. (302°C.) and 650°F. (343°C.) in contact with a body of fuller's earth substantially coextensive therewith, taking off vapours from said body of oil and subjecting them to a refluxing operation, taking off vapours including gasoline components from the refluxing operation, stripping reflux condensate from the refluxing operation of light components, and returning reflux condensate from which light components have been so stripped to the first said body of oil."

B. ORMONT (U.S.P. 1,691,300, Nov. 13, 1928) discloses

"A method of treating a hydrocarbon oil which comprises heating the oil to a temperature sufficient to vaporise the lighter fractions thereof but insufficient to completely vaporise the same; independently heating water to produce a region of nascent steam; regulating the proportion of oil to water, so that with any oil treated the product of the latent heat of vaporisation of the oil and the weight of said oil shall substantially equal the product of the latent heat of vaporisation of the water and the weight of said water; conveying the unvaporised oil to said region of nascent steam where the oil is completely vaporised; and subjecting the resultant mixture of oil vapours and steam to additional heating."

C. L. PARMELEE and E. W. ISOM (U.S.P. 1,675,575, July 3, 1928) cover

"The improvement in the cracking of oil in tubular cracking stills which comprises forcing the oil in a single-pass through a cracking coil and heating the oil therein to a cracking temperature under a high pressure, introducing a solvent oil into the partially cracked oil at one or more intermediate stages of its progress through the cracking coil, and preheating the solvent oil by heat interchange with the cracked oil or with distillates therefrom."

W. C. PARRISH (U.S.P. 1,690,243, Nov. 6, 1928) converts higher boiling hydrocarbons into lower boiling hydrocarbons by a

"Process that comprises maintaining a body of oil at a cracking temperature to cause the formation of lighter hydrocarbons and carbon, agitating said body of oil by means of a power operated agitating means, measuring the power employed in operating said agitating means, and continuing the operation with resultant accumulation of carbon and consequent increased resistance to the movement of the agitating means and stopping the run when the increased resistance, as measured by the amount of power employed in operating the agitating means, reaches a predetermined amount indicating the excessive production of carbon."

H. L. Pelzer (U.S.P. 1,719,486, July 2, 1929) places

"In oil stills in which the charge is circulated through a bed of finely divided material, an improved support for the bed of finely divided material comprising a pair of gratings and an interposed screen, said gratings being made up of strips arranged edgewise with reference to the interposed screen."

W. J. Perelis (U.S.P. 1,701,477, Feb. 5, 1929) claims a

"Process for the conversion by heat of a heavy heterogeneous mineral oil feed stock into gasoline, and higher boiling point products comprising separating the more volatile from the less volatile constituents of the feed stock, subjecting said less volatile constituents to a cracking reaction and separating a heavier fraction of the more volatile products of said cracking, mixing said heavier fraction with a heavier fraction of the more volatile constituents of the feed stock, separately cracking said mixture concomitantly with but under different conditions than said first-named cracking reaction, and collecting the products of said cracking reactions which have a boiling point within the gasoline range."

R. T. Pollock (U.S.P. 1,670,122, May 15, 1928) presents

"An apparatus for treating hydrocarbon oil, including an elongated furnace having a fire box at the lower side thereof, a baffle wall disposed above said fire box, said baffle wall being provided with openings adjacent one end thereof, a plurality of oil heating tubes disposed above said baffle wall, means for introducing oil to said tubes at one end thereof, means for discharging the oil from said tubes adjacent the open end of said baffle wall, a second baffle wall disposed above said tubes, means for conveying combustion gases away from said tubes at the end of said second baffle wall adjacent the inlet to said tubes, a vapour chamber disposed above said second baffle wall, and means for conveying oil from said tubes to said vapour chamber."

R. T. Pollock (U.S.P. 1,676,924, July 10, 1928) covers

"The process of vaporising hydrocarbon oils, which consists in passing oil that has been heated in a furnace to a distilling temperature in a restricted stream through a vaporising zone located outside of the furnace where no rise in temperature of the oil occurs, in releasing vapours from said stream into said zone at different intervals during the travel of the oil through said zone in said restricted stream."

R. T. Pollock (U.S.P. 1,683,801, Sept. 11, 1928) describes

"In an apparatus for cracking hydrocarbon oil, the combination of a dephlegmator comprising an elongated vertical cylindrical shell, partition members located in said shell near each end thereof forming upper and lower compartments and an intermediate compartment, a vapour inlet and a vapour outlet communicating with said intermediate compartment, a plurality of tubes mounted in said partitions and constituting a communication between the upper and lower compartments of said dephlegmator, said lower partition member being provided with apertures through which the reflux condensate formed in the intermediate compartment can pass from said intermediate compartment into said lower compartment, means for feeding raw oil into the upper compartment of said dephlegmator and means for withdrawing said raw oil and reflux condensate from the lower compartment of said dephlegmator."

R. T. POLLOCK (U.S.P. 1,688,830, Oct. 23, 1928) proposes

"A process of cracking oil, consisting in distilling the oil under pressure to cause substantial vaporisation, subjecting the generated vapours to a dephlegmating and condensing action, utilising water and fresh charging oil as a dephlegmating medium by introducing them to the dephlegmating stage in direct physical contact with the vapours, separating the reflux condensate and charging oil from the water and returning the mixture to the still for further treatment, and maintaining a pressure on the entire system substantially above atmospheric."

R. P. POLLOCK (U.S.P. 1,710,068, April 23, 1929) sets forth

"The process of distilling hydrocarbon oil, which comprises heating oil under cracking conditions of temperature and pressure in a coil, in passing the heated oil to a vapour chamber where vaporisation occurs, in introducing the vapours to a dephlegmator, in condensing and collecting the uncondensed vapours passing from said dephlegmator to provide a pressure distillate, in returning said distillate to a zone of redistillation surrounding the dephlegmator and in which zone the distillate is heated by heat absorbed from the vapours passing through the dephlegmator and from products of combustion from the cracking still, and in discharging for condensation and collection the vapours in said zone of redistillation."

R. T. POLLOCK (U.S.P. 1,721,973, July 23, 1929) discloses

"In an apparatus for cracking oil, the combination with a pair of adjacent insulated chambers, of a heating coil in each chamber, the coils in each chamber discharging into the open interior of the adjacent chamber, means for alternately passing oil through said coils and delivering the heated oil alternately to said chambers for vaporisation, means for discharging the vapours from said chambers, and means for heating the oil passing through said coils by igniting carbon accumulating in the enlarged chamber during the alternate use of said chambers as vapour chambers."

G. L. PRICHARD (U.S.P. 1,676,207, July 3, 1928) has invented

"The process of cracking petroleum hydrocarbons which comprises maintaining in a still a body of such hydrocarbons under cracking temperature and pressure while withdrawing and condensing vapours of cracked products, agitating the oil by a stirring device in the still operated by a shaft passing outside the still through a packing enclosed in a closed housing and circulating through the housing a fluid under pressure."

F. M. ROGERS and E. J. SHAEFFER (U.S.P. 1,697,573, Jan. 1, 1929) cover

"A method of distilling hydrocarbon oil for the formation of low-boiling products, which consists in heating such oil under pressure to a conversion temperature, introducing into the vapours evolved by the oil, liquid hydrocarbon oil having approximately the characteristics of the desired products, removing the vapours of the desired products together with the vapours of the oil introduced and returning to the oil undergoing heating condensed products of a higher boiling point than the desired products."

J. M. SCHOONMAKER (U.S.P. 1,678,126, July 24, 1928) claims

"The process of converting relatively high-boiling hydrocarbons to lower-boiling hydrocarbons that comprises heating a hydrocarbon oil to a temperature within its critical cracking range as defined in claim 1, subjecting said oil, while being so heated, to pressure sufficient to prevent substantial cracking in said oil, reducing the pressure on the oil and, simultaneously with said reduction in pressure, adding sufficient heat to the oil to at least restore the heat lost through expansion."

The critical cracking range is defined

"As that temperature range within which cracking can be inhibited by pressure and which exists for 10° F. to 50° F. above the normal cracking range at low pressures of the order of 100 lb. per sq. in.

"Improved results are obtained with increase of pressure up to pressures of the order of 1500 lb. to the sq. in. Further increase in pressure is of less advantage, but I consider that it is within the scope of my invention to employ any pressure in the preheater up to 5000 lb. or more per sq. in."

A. SCHWARZ (U.S.P. 1,691,085, Nov. 13, 1928) covers

"The process which comprises heating heavy oil sufficiently to evolve vapour and violently agitating the vapours and oil while being heated to a cracking temperature by means of an agitator rotating at a speed of about 400 to 600 revolutions per minute thereby forming a vapour-oil emulsion."

A. SCHWARZ (U.S.P. 1,733,135, Oct. 29, 1929) claims a

"Process of producing volatile hydrocarbon distillate and gas from crude petroleum oil which comprises passing separate streams of oil and water in confinement in countercurrent flow and out of direct contact with flue gases of constantly increasing temperatures, preheating said stream of oil and converting said water into steam, superheating the stream of steam and vaporising the oil at points where the flue gases are of sufficient temperatures, removing and condensing vapours of said oil, and reacting on the residual oil with said superheated steam at a point in the flow of said flue gases where the temperature is at a maximum and sufficient to convert a substantial portion of said residual oil into gas.

"In operating the process I have charged a Mexican crude oil with a gasoline content of approximately 5 per cent. and by distilling under reflux at a temperature of 680° F. (360° C.) in the still I have obtained 20 per cent. gasoline with an initial boiling point of 125° F. and an end boiling point of 437° F. I have also obtained 32 per cent. of gas oil with an initial boiling point of 400° F. and an end point of 650° F. While distillation was going on, the residue was continually charged to the retort and a gas was produced."

A. A. F. M. SEIGLE (U.S.P. 1,702,275, Feb. 19, 1929) has designed

"An instillation for the distillation and depolymerisation of liquid hydrocarbons comprising a vertical retort provided with a central heating conduit and a passage for the hydrocarbons formed of a series of annular chambers surrounding said central conduit and arranged to cause the hydrocarbons to traverse said passage in alternately opposite directions, heating means disposed at the upper end of said central conduit, means for supplying, at a pressure substantially equal to the

atmospheric pressure the hydrocarbons to be treated to the lower end of said passage, a number of superimposed expander-coolers, the lower expander-cooler being disposed above the vertical retort, means for connecting the upper end of said passage to the lower expander-cooler, means for connecting said expander-coolers to each other, final cooling and condensing apparatus and means for connecting the upper expander-cooler to said final cooling and condensing apparatus."

The vapours may come in contact with copper, iron, aluminium, nickel, etc., to bring about chemical change.

W. F. Sims (U.S.P. 1,703,550, Feb. 26, 1929) has designed

"An apparatus for cracking hydrocarbon oil, comprising a heating coil, a reacting chamber and a dephlegmating means, serially connected, means for condensing uncondensed vapours issuing from said dephlegmating means, means for collecting the resulting distillate, means for returning regulated quantities of the distillate to said dephlegmating means, to be subjected to redistillation while out of contact with vapours undergoing dephlegmation in said dephlegmating means, means for supplying incoming charging oil in regulated quantities to said dephlegmating means, to aid in maintaining a controlled temperature therein, means for withdrawing unvaporised oil from said reaction chamber, and means for maintaining a lower pressure on the distillate undergoing redistillation in said dephlegmating means than is maintained on the vapours undergoing dephlegmation in said dephlegmating means."

M. J. Trumble (U.S.P. 1,696,658, Dec. 25, 1928) claims

"A process for cracking liquid hydrocarbons under pressure which comprises: flowing said hydrocarbon downwardly in a film over an external vertical surface contained within a pressure chamber; heating said surface internally to a temperature sufficient to cause the cracking of said hydrocarbons; removing the residual carbonaceous products of said cracking action from said surface by a combined mechanical and washing process; removing the vapour products of said cracking action from said pressure chamber, and condensing said vapours."

M. J. Trumble (U.S.P. 1,724,982, Aug. 20, 1929) has developed

"A process of cracking petroleum oils which comprises: advancing successive portions of a movable member repeatedly through a heat-receiving zone and then through an oil-receiving and vapour-evolving zone; projecting flame thereon in said heating zone; delivering oil thereto in said receiving zone; and collecting the evolved vapours from said last mentioned zone—said flame and said oil successively contacting with identical portions of the surface of said member."

L. J. Walsh (U.S.P. 1,725,434, Aug. 20, 1929) presents for cracking oils

"The combination of a heating conduit, a vertical drum about 30 ft. high insulated against material heat loss and connected to receive the discharge from the heating conduit in its intermediate portion, a vapour separator, an outlet pipe leading from near the top of the drum and discharging into the vapour separator, a pressure-release valve in said outlet pipe, and a tar draw-off pipe leading from a point near the bottom of said drum to connect into said outlet pipe at a point not exceeding 2 ft. below the top outlet opening."

F. E. WELLMAN (U.S.P. 1,672,668, June 5, 1928) presents

"Apparatus for treating hydrocarbon oils comprising a retort and heating means therefor, means for taking off vapours from a point near the top of the retort, means for supplying oil to be treated and means for drawing off residuum, both the latter means being at different points near the bottom of the retort, and means for reversing said points of supply and withdrawal."

F. E. WELLMAN (U.S.P. 1,680,580, Aug. 14, 1928) discloses

"The method of treating hydrocarbon oil to produce a lighter hydrocarbon of the same series, which consists in distilling the heavier hydrocarbon in one zone at high cracking temperature and pressure, fractionating all the vapours produced in said first zone in a second zone, conducting off and condensing the vapours from said second or fractionating zone while refluxing to and redistilling the heavier fractions in a third zone at a temperature lower than that in the first cracking zone, separately fractionating in a fourth zone the vapours produced by redistillation in said third zone, conducting off and condensing the light vapours from said fourth zone, returning the heavier fractions from the fourth zone into the third zone, and returning all the heavier fractions from the third zone in liquid phase into the first zone, by gravity, the pressure in both the first and third zones being maintained equal."

R. E. WILSON (U.S.P. 1,712,187, May 7, 1929) presents

"The method of conversion of heavy hydrocarbon oils into lighter hydrocarbon oils which comprises subjecting a body of heavy distillate oil to distillation at a pressure of 4 to 6 atm. and at conversion temperatures, continuing such distillation until substantial conversion of the heavy oil is effected and then unvaporised oil reaches an asphaltene content not exceeding 0·4 per cent., removing such unvaporised oil while at conversion temperature, forcing the withdrawn oil through a confined passage in a heated zone, thereby bringing its temperature to 800° F. or higher, discharging the heated oil into a conversion chamber in which no substantial decrease in temperature of the oil is permitted, and separately withdrawing vapours and unvaporised oil from said conversion chamber."

H. WOLF (U.S.P. 1,711,869, May 7, 1929) claims

"A process for the conversion of high boiling hydrocarbons into those of lower boiling point which comprises the steps of forcing said high boiling hydrocarbons under pressure through a tortuous path in indirect heat interchange proximity to a body of washing oil, conveying the high boiling hydrocarbons from said indirect heat interchange proximity with said body of washing oil through a further tortuous path and simultaneously heating same to a temperature at which cracking of said high boiling hydrocarbons takes place, thereupon reducing the pressure on the cracked liquid hydrocarbons and thus imparting a high speed of flow thereto, introducing the expanded and rapidly flowing cracked liquid hydrocarbons into the aforesaid body of washing oil, thereby heating said washing oil and at the same time cooling said cracked hydrocarbons to a temperature below that at which after reactions can take place, introducing said cracked hydrocarbons into said washing oil in such a manner as to aspirate fresh washing oil into said body, dephlegmating and recovering the vapours and returning the higher boiling hydrocarbons to the process."

AUSTRALIAN PATENT.

(Quoted portions are from Australian Official Journal, Patents.)

ANGLO-PERSIAN OIL CO., E. S. L. BEALE, G. H. COXON and A. E. DUNSTAN (Australian P. 13,783, March 12, 1929) outline

"A process for the pressure cracking treatment of liquid hydrocarbons, and particularly of heavy petroleum and other similar residues, consists in maintaining a relatively high degree of turbulence in the stream or column of liquid in its course under treatment independently of the rate of throughput.

"Oil to be treated is forced by a pump through heated coils at a pressure reaching up to 1000 lb. per sq. in., and then through a cooler, after which the pressure is released and the gas separated. The oil in its course through the coils and cooler is maintained in a highly turbulent state by the surge imposed upon it by the operation of a reciprocating pump, under conditions in which the oil is uniformly heated and heat rapidly transferred, whereby the production of carbon in the treatment is minimised, and that of the small amount of carbon produced a considerable part is withdrawn suspended in the liquid."

CANADIAN PATENTS.

(The quoted portions are from Canadian Patent Office Record.)

J. H. ADAMS (Can. P. 280,585, May 29, 1928) describes

"A process of converting hydrocarbon oils which comprises subjecting the oil locally to a cracking temperature developed by an electrically heated resister immersed in the oil, while maintaining superatmospheric self-imposed vapour pressure upon the oil during conversion, removing the evolved vapours, condensing the heavier constitutents thereof and returning them to the action of the electric resister for further treatment, removing and condensing the lighter constituents of the evolved vapours, and maintaining substantially the same self-imposed vapour pressure throughout the entire operation."

C. P. DUBBS (Can. P. 280,400, May 22, 1928) discloses

"An oil cracking process consisting in continuously advancing a restricted stream of oil through a heating tube disposed within a heating furnace where said oil stream is heated to a cracking temperature, in delivering said stream of oil while at a cracking heat to an enlarged reaction zone without permitting the escape of any fractions of said oil stream, in maintaining a body of heated oil in said reaction zone where conversion thereof occurs under a cracking heat, in promoting the conversion of the oil in said enlarged reaction zone by introducing heated incondensible gases thereto to percolate through the oil body undergoing conversion in subjecting vapours generated from converted oil to reflux condensation, in re-cracking the reflux condensate by introducing the same to the inlet side of the heating coil, and in preventing the return of unvaporised residue from the enlarged reaction zone to said heating coil, and in maintaining a superatmospheric pressure on the oil undergoing conversion in said heating coil and said enlarged reaction zone."

F. B. Fretter (Can. P. 281,675, July 10, 1928) describes

"A method of treating fluid hydrocarbons, which consists in rapidly impelling the treated hydrocarbon through a heater of restricted cross-sectional area by pumping it at a working pressure approximately 1000 lb. per sq. in., and at a mean working temperature of 850° F., more or less, meantime independently impressing upon the hydrocarbon a stabilising pressure invariably in excess of the vapour tension of converted hydrocarbons, permitting the escape from the heater of graduated volumes of the heated hydrocarbon, and separating the heavier and lighter hydrocarbons resulting from this treatment, substantially as set forth."

W. S. Hadaway, Jr. (Can. P. 288,706, April 9, 1929) claims

To convert higher boiling hydrocarbon into lower boiling ones by "a process that comprises continuously passing a stream of oil through a coil while applying heated gases to said coil to thereby raise the oil in transit to approximately a cracking temperature, passing the oil thus heated through an electrically heated conduit arranged to maintain the stream of oil discharged therefrom at a predetermined temperature, and conducting said stream of oil into an enlarged chamber maintained at a cracking temperature under superatmospheric pressure."

F. A. Howard (Can. P. 281,169, June 19, 1928) presents

"The process of pyrogenesis of petroleum products which consists in delivering a stream of products of petroleum, heated to an active cracking temperature, into a primary drum in which the products remain at an elevated temperature, above a cracking temperature but below the temperature at which they are delivered, removing admixed products of conversion continuously from the primary drum and passing them through a secondary drum of similar form, maintaining in the secondary drum a temperature substantially below that in the primary drum, regulating the temperature of the secondary drum by the application of a heat adsorption medium thereto, controlling the temperature of the primary drum by regulated recirculation from the secondary drum, and maintaining a high pressure throughout the entire operation."

F. A. Howard (Can. P. 289,347, Apr. 30, 1929) claims an

"Improvement in cracking petroleum oil, which comprises flowing a stream of oil through a heating zone under conditions to give substantial cracking, then through a digester zone in which the oil is held for a relatively longer time without addition of heat, continuously abstracting oil from said zone, uniting it with the stream of oil from the heating zone, and returning the united material to the digester zone."

J. J. Jakosky (Can. P. 288,568, Apr. 9, 1929) reports a

"Process of cracking petroleum or petroleum products, which comprises heating the material to be cracked to successively higher temperatures in a heating zone so as to successively cracked portions requiring increasing temperatures, while keeping such material under sufficient pressure to maintain the uncracked material substantially wholly in the liquid phase while permitting vaporisation of cracked products, withdrawing vaporised products of such cracking from the liquid material and from the heating zone at a plurality of points of successively higher temperatures so that said vaporised products are removed from the heating zone substantially as soon as formed, and while their temperature is

substantially that at which they are formed, subjecting each portion of vaporised products so removed to a separate precipitating operation to remove liquid particles therefrom, returning liquid material so precipitated from each of said portions to the heating zone substantially at the point at which such portion was removed therefrom, and then recovering said vaporised products."

U. S. JENKINS, N. H. RANSTEAD and W. H. HILDEBRANDT (Can. P. 291,420, July 16, 1929) offer

"The process of obtaining gasoline and other light oils from heavier hydrocarbons which consists in subjecting the latter to a cracking temperature under pressure in a still comprising a closed cyclic channel, including a bank of heating tubes and a superimposed drum connected to a baffle tower, while maintaining a continuous charging of heavier hydrocarbons, accompanied by a positive circulation of the still contents through said channel and a continuous production of light hydrocarbons with continuous partial dephlegmation, and selective release of the desired fractions thereof, and a continuous return to the still in unimpeded or induced flow of the remainder."

J. F. JOHNSON (Can. P. 281,167, June 19, 1928) claims a

"Process of cooling pressure stills and analogous apparatus, comprising atomizing water and causing it to pass through the still in cooling relation thereto."

L. LINK (Can. P. 288,310, Mar. 26, 1929) describes

"An apparatus for cracking hydrocarbons which comprises a still, a series of fractional condensers for receiving vapours from said still, a series of final condensers for receiving vapours from the fractional condensers, connections from the fractional condensers back to the still accumulator tanks for receiving condensate from the fractional condensers, cracking passageways for receiving condensate from the accumulator tanks, and discharge lines from the cracking passageways connected into a perforated pipe in the bottom of the still first mentioned."

R. T. POLLOCK (Can. P. 280,401, May 22, 1928) outlines

"A process of cracking petroleum oil, consisting in heating the oil to cracking temperature in a main cracking zone to cause substantial vaporisation, subjecting the generated vapours to reflux condensing action by passing them directly to a reflux condenser, delivering the reflux condensate to a still where it is subjected to atmospheric distillation to drive off those constituents that are of the desired pre-determined end point, then returning the liquid portions of said reflux condensate to the main cracking zone, maintaining a pressure on said cracking zone and reflux condenser in excess of 50 pounds to the square inch, and in heating said atmospheric still."

G. L. PRICHARD and H. HENDERSON (Can P. 285,364, Dec. 4, 1928) report

"A process for the cracking of petroleum oils, which comprises establishing and maintaining a substantially vertical column of liquid oil and over-lying oil vapour in substantially unobstructed communication at cracking temperature and under cracking pressure, preventing substantial loss of heat by radiation from the liquid oil of said column and causing cooling of the vapours of said column to produce a limited degree

of condensation, and delivering heat to said liquid oil by cyclic circulation of oil therefrom to heating means and back to the column of liquid oil, while removing and condensing uncondensed vapours from the vapour overlying the column of liquid oil, and while delivering under pressure additional oil to the column of liquid oil after first passing said additional oil down through the vapours arising from the column of liquid oil."

N. H. RANSTEAD (Can. P. 292,574, Aug. 27, 1929) describes

"A process of obtaining gasoline and other light oils from heavier hydrocarbons which consists in continuously subjecting the latter to a cracking temperature under pressure in a still compriaing a closed cyclic channel, while maintaining continuous charging of raw material, continuous production of desirable light hydrocarbons, combined with continuous or substantially continuous rejection of a portion of the still contents with intermittent forcing of corrective material into that portion of the still from which the reject is taken, accompanied by a simultaneously positive circulation of the entire still contents."

S. SCHWARTZ (Can. P. 285,472, Dec. 11, 1928) describes

"A method of producing petroleum distillates, which comprises the feeding of a suitable cracking stock to a cracking still wherein a cracking temperature and pressure are maintained, withdrawing vapours from said still and subjecting said vapours to fractional condensation of such degree that the uncondensed vapours have a lower end boiling point than that of the distillate desired, withdrawing the condensate resulting from said fractional condensation and subjecting said condensate to fractional distillation, the heat for such fractional distillation being obtained by withdrawing the liquid residue from said cracking still, releasing the pressure on said residue, collecting the resulting heated vapours and transferring the heat from said heated vapours to said condensate for the fractional distillation thereof."

A. C. SPENCER and E. W. LUSTER (Can. P. 292,034, Aug. 6, 1929) present a

"Method of cracking hydrocarbon oil, comprising heating the oil to a cracking temperature in a coil, fractionating the cracked oil product, collecting from said fractionating operation a heavy condensate containing dissolved low boiling hydrocarbons, separately heating said condensate by the source of heat for said coil, and returning the heated condensate to the fractionating operation, wherein low boiling hydrocarbons escape from the condensate without material cracking, with drawing vapours, and condensing the same."

S. STRANSKY and F. HANSGIRG (Can. P. 285,060, Nov. 27, 1928) present

"A process for cracking hydrocarbons by a distillation continuously effected under a self-imposed pressure and under reflux condensation, characterized by the feature that a permanent free escape of the evolved vapours of desired volatility from the vapour space of the retort is allowed to take place independently from the pressure existing therein, and that by the supply of the quantities of heat required for vigorous distillation of the formed low boiling point hydrocarbons by means of large heating surfaces, the temperature of which does not considerably exceed that of the liquid to be heated, the equilibrium within the liquid phase is permanently disturbed so that the splitting is proceeding at the lowest temperatures and pressures sufficient for initiating the cracking of the raw material under treatment without any far-going decomposition taking place."

L. J. Walsh (Can P. 285,669, Dec. 18, 1928) claims a

"Process for cracking liquid hydrocarbon material, comprising causing the material to flow in a stream of uniform volume of flow, impressing upon said stream cracking temperatures for the production of gasoline volatiles in separated zones in succession, causing recession of temperature intermediate said heating zones, withdrawing vaporised products from said stream during said recession of temperature and maintaining the volume of flow by additions of fresh material to the vaporising materials intermediate the heating zones."

ENGLISH PATENTS.

(The quoted portions of English patents are from the Illustrated Official Journal.)

Anglo-Persian Oil Co., Ltd., Beale, Coxon, and Dunstan (E.P. 293,889, Sept. 5, 1928) impart a

"High degree of turbulence to the stream of hydrocarbons flowing through a cracking coil by causing the stream to move in surges generated by a reciprocating pump. The oil is pumped through a coil by a pump under a pressure of 1,000 lbs. per square inch, the temperature being gradually increased from 380—450° C., and then diminished to 400° C., the products finally passing through a cooler at 250° C. The coil comprises seven sections, each 6 ft. long and 1 in. in diameter, each section being connected by two right-angled turns, and the ends of the coil are connected to the pump by pipes."

C. Arnold (E.P. 286,917, May 2, 1928) provides that

"In a process for cracking hydrocarbon of the kind in which the crude oils are rapidly heated in the liquid phase under pressure without substantial decomposition, and are then passed into a cracking zone where decomposition takes place, the cracked oils being finally allowed to vaporise by reducing the pressure, the cracking zone comprises a series of converters through which the oils are passed at slow speed without distillation, while maintaining the temperature and pressure and which are arranged so that any chamber may be cut out without disturbing the continuity of the process."

C. Arnold (E.P. 296,919, Oct. 31, 1928) has devised a process in which

"Petroleum oils to be cracked and fractionated are passed through a heating apparatus such as a bank of tubes, a heat-retaining passage way such as the lagged drum, and a number of fractionating towers, connected in series, the last tower receiving vapours at or near the middle of its height from the preceding tower and having at its upper end means for controlling reflux which are independent of the supply of oil to be cracked. Both towers have controlled cooling coils at their upper ends, and the final tower has also a heating coil. A pressure release valve is interposed between the cracking drum and the fractionating towers."

C. Arnold (E.P. 299,683, Dec. 28, 1928) provides that

"In liquid phase cracking processes of the tube and digestion drum type, in which pairs of digestion drums are employed so that one may be used while another is being cleaned, the drum which has just been cleaned is filled with heated oil before diverting the stream of oil passing to the drum still in use."

C. ARNOLD (E.P. 302,211, Feb. 6, 1929) arranges that

"In a process of cracking oils employing plant similar to that described in Specification 274,763, comprising a cracking coil, digester drum, still and dephlegmator, the crude oil is first injected into the still through a pipe where it is vaporised, the vapours are fractionated in the dephlegmator tower, and the condensate collecting at the bottom of the tower is led through pipes to the cracking coil and digester, the cracked products being injected directly through a pipe into the tower or alternatively through a pipe into the still. The residual oil in the still is led off through a pipe to storage or is passed to the cracking coil through a valve and the pipes. An intermediate fraction may be collected in the pan in the tower, and this fraction is led off to storage through a pipe or returned to the still by a pipe. The plant is adapted for cracking (1) a low-grade stock tending to deposit carbon in cracking—*e.g.*, Smackover crude, in which case the crude oil is injected directly into the still and only the condensate obtained in the tower is passed through the cracking coil, the cracked products being injected into the still; (2) a feed stock—*e.g.*, Panuco crude, which does not tend to deposit so much carbonaceous matter, in which case also the crude stock is passed directly to the still and the residual oil therefrom is passed through the valve to the cracking coil and digester, the cracked products being injected directly into the tower; (3) gas oil which is stripped in the still under pressure, the residuum from the still being cracked as before and injected into the tower, where condensate is collected in the pan and returned to the still through the pipe. The digestion drums may be in duplicate."

C. ARNOLD (E.P. 302,415, Feb. 6, 1929) claims that in

"A process for cracking oils in which the oil is conducted under pressure and at high velocity through a heated coil from which it flows into a digestion drum maintained at the same temperature and pressure, the temperature of the oil in the digestion drum is controlled by introducing relatively cool oil into the drum at the same point as the heated oil enters."

C. ARNOLD (E.P. 311,362, July 3, 1929) describes

"A process for cracking oils of the type comprising a heating coil and a digestion drum maintained under the same pressure in which the temperature of the oil in the digestion drum is controlled by partially condensing the vapours formed in the drum in a tower maintained under the same pressure and returning the condensate through a pipe into admixture with the oil passing from the coil to the drum at a point anterior to that at which it enters the drum through the pipe. The uncondensed vapours from the tower and the residual liquid in the drum are mixed, after passage through pressure-reducing valves in a pipe and discharged into a separator in which vaporisation is aided by a steam spray. The uncondensed vapours pass to a condenser while the condensate produced by the cooling coil, and the tar collecting at the bottom of the separator are removed through pipes. The amount of condensate formed in the tower is controlled by a cooling coil through which the crude oil may be passed on its way to the coil. The coil, drum, and tower are maintained under a pressure of about 350 lbs. per square inch."

C. ARNOLD (E.P. 313,057, July 31, 1929) lines

"Oil distillation and cracking apparatus, such as 'soaking drums' used in the tube-and-tank process with non-corrodible metal applied by fusion plating. High chromium steels are especially suitable—*e.g.*,

an alloy containing 70—73 per cent. iron, 16—18 per cent. chromium, 1·25—1·75 per cent. silicon, and about 0·10 per cent. carbon. The plating is effected by attaching a wire strip or plate which forms the electrode in an electric arc welding method. The drum may be rotated during the building up of the plating on its cylindrical wall."

J. BETHENOD (E.P. 316,905, Oct. 2, 1929) decomposes

"Liquid hydrocarbons such as petroleum and coal tar oil by electrical conductors of high melting-point heated to a temperature above 800° C., means being provided for preventing deposition of carbon on the conductors and for circulating the hydrocarbon under treatment."

G. FACHINI (E.P. 316,520, Sept. 5, 1929, not yet accepted) claims a process in which

"Oils are cracked and distilled by feeding them into a chamber filled with refractory material maintained at a sufficiently high temperature. The apparatus is stated to be suitable for use with internal-combustion engines running on heavy oils, the exhaust gases then being used to heat the cracking vessel."

GASOLINE PRODUCTS CO. and G. C. HARGROVE (E.P. 290,996, July 18, 1928, not yet accepted) control

"The conditions of temperature, pressure and time in the cracking operation so that not more than 25 per cent. of the crude oil is converted into gasoline in a single passage through the apparatus. The process is preferably continuous, the fresh feed of crude oil being diluted with preferably twice its volume of the clean overhead distillate produced."

H. A. GILL (E.P. 297,949, Nov. 21, 1928) presents the improvement

"In a process for cracking oils of the kind in which oils are passed in the liquid phase through a heating zone to a conversion chamber, from which the cracked products flow to an evaporating chamber through a reducing valve, the vapour produced passing up to a dephlegmator, evaporation in the chamber is checked and controlled by introducing through a pipe a cooling oil which, mixing with the cracked products, prevents excessive vaporisation and the formation of coke-like or asphaltic 'bottoms.' The residues from the chambers pass by pipes through a condenser to storage towers, while the vapours passing from the top of the dephlegmator through a pipe are condensed in the condenser and stored in a tower, the gases formed in the cracking being separated in a separator, and led off through a pipe. Alternatively the residues from the tower are collected in a chamber and returned with the crude oil to the heating zone."

KNOWLES AND ANDREWS (E.P. 311,689, July 10, 1929, not yet accepted) state that

"In dehydrating, distilling and cracking tars, pitches and other hydrocarbons—*e.g.*, those derived from coal, lignite, wood, or petroleum oils, the liquid material passes from a header through nozzle tubes into chambers containing baskets preferably filled with loose coke, etc. The liquid falls thence on to the heated floor of a heating chamber of aluminium oxide brick or refractory glass, a rotary basket containing loose coke, etc., being in some cases interposed through the axle of which steam or gas may be introduced through a pipe."

H. MAGNUS (E.P. 287,525, May 16, 1928, not yet accepted) provides that

"Mineral oils and tars are distilled under pressure and the products are separated in a condensation plant into fractions of higher and lower boiling point than gasoline, the fraction of higher boiling point, being then further treated under higher conditions of temperature and pressure in a cracking apparatus."

H. MAGNUS (E.P. 313,937, Aug. 14, 1929, addition to E.P. 287,525) states that

"In the process of continuous distillation and cracking of mineral oils and tars described in the parent Specification the process is carried out using heated reaction vessels in which the surfaces from which heat is emitted are arranged to be larger than those on which heat is absorbed by constructing such surfaces with corrugations, ribs, fins, etc."

A. H. MARKS and P. RUSSELL (E.P. 316,600, Sept. 25, 1929) devise

"A process for cracking heavy hydrocarbons in which the heating, conversion and separation zones are entirely separate, and the heating zone is divided into two parts such that the heat supplied per unit length up to the point at which the lowest cracking temperature is reached (about 390° C.) is less than the heat at the end of the heating zone where the desired cracking temperature is attained."

R. T. POLLOCK (E.P. 287,344, May 9, 1928) provides that

"In a cracking process of the kind in which the oils are cracked under pressure in pipes and then passed to a reaction chamber from which the vapours produced are passed through a dephlegmator, the temperature of which is controlled so as to condense the insufficiently cracked oil, the condensate is passed to a still in which the lighter fractions are evaporated by heat other than that of the treated oil—*e.g.*, by the hot gases from the furnace passing up a flue. The residue in the still is returned to the pipes through a pipe by a pump. The crude oil is first passed down the dephlegmator from a pipe or alternatively is fed directly to the coils through a pipe. The vapours from the dephlegmator are passed through a condenser to a storage tank while the vapours from the still pass to a condenser and tank. The coils are maintained at about 900° F. with a pressure of 150 lbs. per square inch."

RISPLER (E.P. 305,263, Mar. 27, 1929) distills

"Oils, tars, and like carbonaceous liquids with the simultaneous separation and reduction to powder of their non-volatile contents, by passing them through a pipe into a rotary still containing iron balls and like crushing material and heated in a furnace. The temperature of the still is sufficient to cause immediate vaporization of the volatile constituents, the heavy asphaltic portions and the carbon being deflected by a baffle and dropping on to the crushing members where they are reduced to a powder and deprived of any remaining volatile contents. Steam is preferably blown into the still through a pipe and an annular passage surrounding the pipe. The steam aids the distillation and is also used for blowing out the dried powder accumulating in the still, which for this purpose is provided with a conical end. The vapours produced are led off to the usual condensers through a pipe. Alternatively the powdered residue may be evacuated by placing a grating over the charging hold and rotating the still."

SACHANEN and TILITSCHEYEW (E.P. 307,105, May 1, 1929) provide that

"In a process for cracking oils in which the oils are forced through a pre-heating coil and a cracking coil, the diameter of the pipes of cracking coil being considerably greater than that of the preheating coil, the coils are arranged in the same chamber and the cracking products are led through a reducing valve to an expansion chamber maintained under atmospheric pressure where carbon is deposited. The vapours produced pass through a pipe to a dephlegmator through the top of which the crude oil is circulated and thus preheated. The condensate collecting in the bottom of the dephlegmator is partially re-evaporated by heat interchange with the cracked products passing through a coil. Residues remaining in the vessels may be recycled through the system by a pump. The chamber is provided with non-perforated trays. Further preheating of the crude oil is obtained by passage through a heat interchanger through which the hot residues from the vessel are also circulated. The rate of flow through the reaction and heating tubes should not be less than 0·5 and 2 metres per second respectively."

SINCLAIR REFINING COMPANY and E. C. HERTHEL (E.P. 303,879, Mar. 6, 1929, not yet accepted) prescribe that

"In a process for cracking oils of the kind in which oil is circulated under pressure through a tubular heating zone and a vapourising zone comprising a drum from which the vapours pass through a dephlegmator tower to a condenser and separator, the oil is circulated continuously with the continuous addition of fresh oil through a pipe until the concentration of pitch in the cycle nearly reaches saturation. The circulation is then stopped by closing a valve in the circulation member, but the cracking is continued by still supplying fresh oil while removing a corresponding amount of pitch laden oil from the system through a pipe. The fresh oil, together with condensate formed in the tower, is admitted to the member through a pipe. A pressure of 125-300 lbs. per square inch is maintained in the whole system by a valve. A pipe is provided for filling the apparatus at the commencement of the operation and the heated gases may be recirculated over the cracking tubes through a pipe."

A. D. SMITH and J. PERL (E.P. 289,673, June 20, 1928) present the invention that in

"A process for cracking oils in which the oils heated in the liquid phase by passage through pipes in a furnace are allowed to expand in a still, the unvaporised residue passes through a pipe to a heat-exchanger where it is cooled by heat exchange with the raw oil to cause precipitation of the heavy polymerised products which are separated by gravitation in the tank. The lighter fractions pass through a line to cracking tubes, when they are re-cracked and the products mixed with those passing from the first mentioned tubes. Evaporation of the cracked oils in the still is controlled by hemispherical perforated conversion plates rotatable by a handle through a chain and gear wheels."

STANDARD OIL DEVELOPMENT CO. (E.P. 295,399, Oct. 3, 1928, not yet accepted) provides that in

"A process for cracking oils by the tube and drum method condensate from an intermediate stage of the process is led away, reheated and returned to the point from which it was taken."

STANDARD OIL DEVELOPMENT COMPANY (E.P. 304,798, March 20, 1929, not yet accepted) arranged that

"Oils are cracked by an apparatus of the coil and drum type, the cracked material being withdrawn and mixed with uncracked oil, and separated from tar and fractionated."

TRENT PROCESS CORP. (E.P. 313,159, July 31, 1929, not yet accepted) devises a method by which

"Oils are cracked by passing them from a main supply pipe through a tube and radially arranged tubes into a rotating cylinder heated by hot flue gases passing from a fire box into a fixed box delivering to a hollow tube and thence through radial tubes to the space formed between the cylinder and stationary outer casing. The oil is thus heated in bulk form by the tubes in their lower arcs and in film form in their upper arcs. The vapours produced are led off through pipes. A plug prevents the oil flowing beyond the intake pipe and a second plug directs the flow of vapours outwardly. The flue gases are recircuited by a pipe through a heat exchanger back to the box. The tubes may be cleaned by removal through plugs, and may be covered with glass, porcelain, silica or other materials which have a selective attraction for water in preference to oil. The oils used may contain solid carbonaceous material in suspension."

FRENCH PATENTS.

ANGLO-PERSIAN OIL CO. (F.P. 655,823, May 15, 1928) provides that

"During cracking, liquid hydrocarbons, particularly petroleum, are given a relatively high degree of agitation, which may be caused by a pump imparting eddy or wave motions to the oil during its passage through the apparatus."

BLÜMNER CRACK-ANLAGEN A.-G. (F.P. 657,949, July 21, 1928) presents

"An apparatus in which oils to be cracked are given a whirling movement in the heating tubes."

I. G. FARBENINDUSTRIE A.-G. (F.P. 653,646, May 1, 1928) produces olefins, etc.

"By heat decomposition of paraffins in a furnace of which the hot parts are made from alloys of metals of the iron group among themselves or with common metals at the large minima of the curve of atomic volumes of the elements, or with alloys of the latter with other metals; or the hot parts of the furnace are made of materials which provoke abundant deposition of carbon, and these are coated with preserving substances."

JENKINS PETROLEUM PROCESS CO. (F.P. 659,949, Sept. 4, 1928) devises

"An apparatus in which a heavy hydrocarbon is carried to cracking temperature under pressure in a heater forming a closed cycle and which contains a group of heating tubes, a cylinder placed above the tubes and a baffle plate tower joined to the upper part of the cylinder, the residual products from the tower being mixed with fresh material and returned to the cylinder."

JENKINS PETROLEUM PROCESS CO. (F.P. 653,916, May 5, 1928) cracks

"Heavy oils by circulating them rapidly by forced circulation in a tubular heater while imparting a whirling movement to the oil so that at each passage through the tubes the crude oil is heated only a little at a time and the loss of heat from one passage to the next is negligible so that the temperature, pressure, dispersion of solids and liberation of gasoline vapours are constant throughout the heater."

STANDARD OIL DEVELOPMENT CO. (F.P. 658,721, Aug. 8, 1928) describes a

"Plant for cracking oils in which the oil is heated to cracking temperature in a worm, the cracked product being transferred at an intermediate part to a fractionating zone, from which the condensed liquid is withdrawn and heated by a source of heat exterior to this zone and brought back to the fractionating zone."

GERMAN PATENT.

SINCLAIR REFINING CO. (D.R.P. 475,836, May 4, 1929) reports a

"Process of cracking hydrocarbons by vaporising and distilling oil under pressure in pipes heated by flue-gases. The pipes are supplied from the lower part of a container having a sieve and a layer of absorbing material. As the oil above the sieve becomes rich in tar, it is removed and fresh oil added so that the tar content never approaches the saturation point."

NEW ZEALAND PATENT.

DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ (New Zealand P. 63,565, Oct. 31, 1929) claims

"An invention for treating hydrocarbons characterised by the material that is to be treated being circulated through a system consisting mainly of heating tubes—for instance, a tube furnace and a vapour separator connected therewith in which latter the vapours and gases developed by the reaction, also vapours or gases not absorbed by the material, are separated, whereby the material in the feed-line to the tubing system and/or in the tubing system itself is brought into contact with the gases or vapours, whilst the treated material with the desired properties is carried off from the vapour-separator in a continuous manner. The invention is further characterised by the material in the vapour-separator also being brought into contact with the gases or vapours."

Indirect Heating.

UNITED STATES PATENTS.

C. R. DOWNS (U.S.P. 1,708,303, Apr. 9, 1929) heats petroleum products in cracking

"By means of the vapours of boiling sulphur out of direct contact therewith but in heat transferring relation thereto and regulating the temperature of the said sulphur vapours by the pressure applied thereto."

F. A. HOWARD (U.S.P. 1,686,490, Oct. 2, 1928) cracks hydrocarbon oils

"In a cycle of successive operations, comprising charging the hydrocarbon oil into a plurality of distillation vessels, contacting said vessels in rotation with a molten bath maintained at a high temperature, collecting distillate, breaking said contact as soon as the distillation is substantially complete, cleaning said vessels and recharging the same with hydrocarbon oil in rotation."

A. E. PEW AND HENRY THOMAS (U.S.P. 1,692,786, Nov. 20, 1928) claim

"The process of cracking mineral oil which comprises heating a body of liquid mercury under an absolute pressure required to produce mercury vapour at a temperature above that at which substantial cracking of the oil will occur, but below that required to form any substantial amount of coke, establishing a flowing stream of oil of great length and small thickness at a temperature below that of the mercury vapour and flowing the mercury vapour into a confined space surrounding the flowing elongated stream of oil and into heat exchange relation with the oil to effect condensation of mercury vapour and such transfer of its latent heat to the oil as will decompose higher boiling constituents thereof into lower boiling products, returning the condensed mercury to the body of liquid mercury, and continuously removing the oil from the locus of heat exchange."

The cracking tubes are "maintained throughout at a high pressure, say, 600 lb. per square inch."

"The mercury boiler may be operated at a pressure of about 80—85 lb. gauge pressure, which will give a mercury vapour temperature of about 900° F."

PATENTS OF OTHER COUNTRIES.

H. MAGNUS (Australian P. 12,929, Jan. 15, 1929) states that

"To continuously distill and crack mineral oils and tars in two or more stages, the stages are combined into a single operation so that the distillation vapours are condensed into fractions of higher and lower value, respectively, than gasoline, and the former are withdrawn, while the latter are fed, either in the form of vapour or liquid, into a cracking apparatus.

"Raw oil is pumped from a pipe through heat exchangers, pipe, and nozzles into a distillation vessel containing a body of molten metal. Vapours and gases pass through a pipe and turbine into a condenser, and condensates are withdrawn through a pipe and non-condensable fractions are returned to the vessel."

F. A. HOWARD (Can. P. 284,608, Nov. 6, 1928) reports a

"Process of cracking hydrocarbon, comprising heating in a closed system a substance which at a temperature of 700° to 1,000° F. exerts a pressure of less than 200 lb. per square inch, and is stable against decomposition at such temperatures, subjecting the hydrocarbon to indirect heat of the vapours of such substance within the temperature range specified, whereby the hydrocarbons are cracked by uniformly applied heat, taking off vapours, cracked products, and condensing the same."

Howard claims also a "process of cracking hydrocarbons, comprising heating mercury in a closed system to a temperature above 700° F.,

subjecting the hydrocarbons to indirect heat of the mercury vapour at such temperature, whereby the hydrocarbons are cracked by uniformally applied heat, taking off vapours, cracked products, and condensing the same."

P. D. HAHN (E.P. 289,482, June 20, 1928) effect preliminary

"Vaporisation by passing heavy oils through a molten metal bath, decomposes with steam at 350—360° C., as in E.P. 235,625, and condense the light hydrocarbons."

J. H. JANSEN (D.R.P. 456,312, May 3, 1928) presents a

"Process in which mineral oils in liquid or vapour form are led through a bath of metals or metal salts at cracking temperature at such a rate that the carbon formed is carried out in suspension in the vapours.

Treating Charging Stock before Cracking.

ROY CROSS (U.S.P. 1,718,218, June 25, 1929) presents

"A process of producing refined gasoline, which consists in preliminarily treating a hydrocarbon charging stock suitable for cracking in successive steps with a sodium plumbite solution and with sulphuric acid, and subjecting the oil to a cracking action for separating out the gasoline content."

"A typical result of this method of treatment is shown by the following sulphur contents at different stages:

	Per cent. sulphur.
1. Raw oil	2·75
2. Oil treated with doctor solution	2·50
3. Oil treated with sulphuric acid	0·35
4. Synthetic crude oil	0·30
5. Raw cracked gasoline	0·12
6. Gasoline treated with sodium plumbite and filtered	0·05

The same raw oil, cracked without preliminary treatment, gave the following results:

	Per cent. sulphur.
1. Raw oil	2·75
5. Raw gasoline	0·70
6. Gasoline after treatment with sodium plumbite ..	0·60

(*d*)—*Corrosion of Cracking Equipment.*

Egloff[66] emphasises the seriousness of the corrosion of pressure still equipment with the ever-increasing cracking of high sulphur oil. He outlines the success achieved to date in combating corrosion by the use of non-corroding metals, non-metallic linings, chromium plating and the injection of chemicals. He states that chrome nickel steel has been used successfully as non-corroding

[66] World Engineering Conference, Tokio, Japan, Oct.-Nov., 1929.

tubes for pressure stills. Some tubes of this material have successfully resisted over 4,000 hours of service, using high sulphur California cracking stock.

A successful protection for reaction chambers is the so-called "Ganister" lining. Expanded metal is fixed to the walls of the chamber and a mixture of cement and Ganister (crushed fire brick) applied with a spray gun.

A second kind of non-metallic lining successfully used to protect reaction chambers described by Morrell, Faragher, and Mekler[67] is made of fire clay, sand, and asbestos with water glass as a binder. The lining is applied directly to the chamber wall and cured by slow heating to 900°F. to dehydrate the sodium silicate.

Jasper[68] states that alloy steels high enough in chromium and nickel to be corrosion resistant are too expensive for use in building reaction chambers, and he believes that metal linings in the places exposed to corrosion should be relied on for protection. Corrosion is accelerated by high pressure and high stress, but does not necessarily increase with rise in temperature.

Faragher[69] summarises the progress that has been made in combating corrosion of pressure stills.

Snyder and Brett[70] states that a chrome nickel steel is giving satisfactory resistence to corrosion in the tubes of cracking stills.

Hall and de Taveau[71] show that cracking gives rise to volatile organic acids, notably acetic and propionic acids, and to these they attribute some of the corrosion of cracking equipment.

Faragher, Morrell and Comay[72] find that while mercaptans, sulphides, and disulphides decompose at cracking temperatures, whether alone or dissolved in gas oil, thiophene is stable at 1,600° F. (871° C.). A cracked naphtha containing no hydrogen sulphide, elementary sulphur, mercaptans, sulphides, or disulphides and containing 0·81 per cent. sulphur formed substantially no sulphur decomposition products at 496° C. (925° F.). The residual sulphur, therefore, acted as thiophene. "The stability of thiophene suggests the reason why certain crude oils or fractions, while high in sulphur content, cause less corrosion during cracking than other types of a much smaller content of sulphur. Smackover crude, containing 2·5 per cent. of sulphur, shows less corrosion during the cracking operation than Panhandle crude, containing 0·6 per cent. of sulphur."

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[67] *Oil Gas J.*, Dec. 6, 1928, 55.

[68] *Oil Gas J.*, June 7, 1928, 205.

[69] *American Petroleum Institute Bull.* **10**, No. 2, 102 (1928). *Petr. Times*, 1929, **21**, 43.

[70] *Nat. Pet. News*, Oct. 30, 1929, 126.

[71] *Oil Gas J.*, Dec. 6, 1928, 110.

[72] *Ind. Eng. Chem.*, 1928, **20**, 527.

PATENTS.

O. E. Andrus and Sune Hermanson (U.S.P. 1,680,276, Aug. 14, 1928) cover

"The method of lining vessels, which comprises the operations of securing a liner within the vessel by disposing a thin imperforate sheet of corrosion resisting alloy against the inner wall of the body of the vessel, and bonding the said liner to the said body by electrical welding at frequent and contiguous points through the liner without changing the nature of the liner, to thereby prevent distortion of the liner from its position in the vessel by temperature differences and provide for an increased transference of heat between the liner and the body of the vessel."

Henry H. Hewetson (U.S.P. 1,707,520, Apr. 2, 1929) utilises in the protection of cracking reaction chambers

"The observed immunity from corrosion of such parts of such containers as are continuously covered by liquid to prevent any necessity for replacing any part of the large vessel itself."

and he covers

"The combination of a container for oil adapted to receive and hold contents at pressures of several hundred pounds to the square inch and temperatures of the order of 450° to 900°F., with means for maintaining the whole interior surface of said container in contact with oil in a liquid state comprising a removable extension at the top of the container into which the liquid oil extends during use of the said container, and means connected with the said extension for drawing off oil therethrough, and an educt passage in said extension communicating with a vapour space in said extension above the oil."

J. C. Morrell and H. P. Benner (U.S.P. 1,715,095, May 28, 1929) claim

"A method for preventing corrosion of the condensing portion of an oil cracking apparatus, consisting in introducing ammonia in solution to the vapours subsequent to the heat treatment thereof and prior to their passage through the condensing portion of the apparatus whereby the ammonia solution is not subjected to the oil cracking conditions, to effect a neutralisation of the hydrochloric acid contained in the vapours formed during the cracking reaction in the apparatus."

A. C. Holzapfel (E.P. 291,585, July 25, 1928) protects

"The interior surfaces of oil-cracking retorts by applying a paint-like composition comprising water-glass, water, a powdered solid alkaline earth (including magnesia) or compound of alkaline earth, and one or more powdered inert refractory mineral substances, and subjecting the coating to an oil cracking temperature such as 900°F. upwards. A preferred composition comprises magnesite and/or slaked lime, with or without an inert pigment such as titanium oxide, fireclay being used as the refractory material."

Standard Oil Development Co. (Fr. P. 648,965) states that

"Corrosion resisting lining for high pressure cracking chambers, is obtained by welding on the inner surface of the vessels a continuous band of several layers of corrosion resistant metal or alloy preferentially chromium steel."

(e)—*Stabilisation of Cracked Distillates.*

Burrell and Mase[73] present an apparatus for stabilising cracked distillate by removing fixed hydrocarbon gases from it, and at the same time separating a light gasoline fraction which does not require acid treatment, because colour, gums, and odorous compounds concentrate themselves more or less in the heavier portions of the oil. The pressure distillate is expanded into the upper portion of a degassing column at about 30 pounds pressure. The gas leaves overhead, reflux oil which collects in the bottom is heated and finally passes to a second tower for fractionation, a light oil fraction leaving the top of the second tower. If a vapour recovery system is not used, the full pressure of the cracking system, for example 175 lbs., is used, and the overhead gas is contacted with heavy pressure distillate to remove gasoline as cleanly as possible. In some refineries the pressure used on the stabiliser is higher than on the cracking system, but Burrell and Mase feel that the pumping and heating cost which this entails is unnecessary.

Wilde, Meade and Coleman[74] stabilise pressure distillate by use of a single tower operating at 120 lbs. in which the pressure distillate is introduced at a mid-point, gas leaves the top of the tower, and heat is applied to control the temperature of the condensate at the bottom of the tower.

PATENTS.

E. H. Leslie and E. M. Baker (U.S.P 1,684,771, Sept. 18, 1928) patent in

> "... A process of obtaining valuable products from mineral oil, the steps which comprise conducting superheated hydrocarbon vapours from a vapour phase cracking plant into the lower part of a fractionating column and effecting countercurrent contacting between such vapours and a liquid condensate, and refluxing to the upper part of said column a substantial portion of the vapours leaving said column, thereby providing liquid condensate for said countercurrent contacting."

G. H. Taber, Jr. (U.S.P. 1,705,077, Mar. 12, 1929) presents

> "An improvement in cracking hydrocarbon oils which comprises subjecting the gas-vapour mixture from the cracking operation to a fractionating operation and then subjecting the remaining gas-vapour mixture to a condensing operation, subjecting the gas-vapour mixture remaining uncondensed from the condensing operation to scrubbing treatment with a higher boiling oil fraction from the fractionating operation, and reintroducing the oil containing constituents absorbed from the gas-vapour mixture in the scrubbing operation into the fractionating operation."

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[73] *Nat. Petr. News*, Oct. 30, 1929, 60.
[74] *Oil Gas J.*, Oct. 3, 1929, 222.

J. W. WADSWORTH (U.S.P. 1,692,476, Nov. 20, 1928) covers

"... . Cracking the oil under heat and pressure to produce a mixture of gasoline hydrocarbons, hydrocarbons lighter and heavier than gasoline hydrocarbons, and residuum, rectifying said mixture to sharply separate the gasoline hydrocarbons and lighter hydrocarbons from heavier hydrocarbons and residuum, subsequently rectifying said gasoline hydrocarbons and lighter hydrocarbons, and separately withdrawing from the second rectification step, rectified liquid gasoline and uncondensed gases, and utilising during the rectification steps, the pressure resulting from the cracking step to effect the second rectification at superatmospheric pressure and at temperatures from substantially atmospheric upwardly."

(*f*)—*Automatic Control of Cracking Units.*

Bradley[75] describes the de Florez regulator for cracking units. He states that the fuel supply going to a cracking unit can be regulated so as to give a maximum temperature variation of 5° F. and that bubble towers can be regulated to 6° F. He also describes an automatic temperature control for the liquid in the bottom of a cracking still stabiliser.[76]

ENGLISH PATENTS.

MAGNUS H. (E.P. 307,511, May 1, 1929) provides that

"In apparatus for the cracking of hydrocarbons, the temperature of the heating zone is automatically maintained constant by thermostatic devices controlling the supply of raw material to this heating zone. Cold oil passes from a tank by way of a pump and cock to a coil and nozzle immersed in molten metal in a vessel. The oil may pass alternatively by a pipe to a preheating coil and a hot oil container, from which it is pumped by a pump through a cock to the cracking vessel as before. A thermostatic control immersed in the molten metal controls through relays of known type the cocks, so that a rise of temperature opens the one cock and partially closes the other cock, thereby supplying a colder raw material."

(*g*)—*Residues from Cracking.*

There has been an increased effort to give greater commercial value to the residual oil, tar, or coke produced by the cracking process. Goodwin[77] describes a process for removing solids and producing a saleable fuel oil from pressure still residues. These solids consist of carbonaceous material and calcium sulphide when lime has been used to check corrosion. The cracked residue is cooled to about 275° F., treated with spent acid, to flocculate

[75] *Nat. Petr. News*, Oct. 17, 1928, 112.
[76] *Nat. Petr. News*, Oct. 30, 1929, 179.
[77] *Nat. Petr. News*, May 15, 1929, 80.

the solids present, which are then separated from the oil. These solids may be filtered, giving additional oil and a filter cake which is a good fuel, and may be briquetted. This process is said to extend the limits to which cracking may be pushed without making unsaleable residuum, to reduce the necessity for the use of crude-still bottoms for blending, and to make possible a freer use of lime to prevent corrosion.

Johnston and Farrell[78] report that pulverised cracking still coke mixed with acid sludge, briquetted, and carbonised at 350–1100° F. makes a saleable domestic fuel.

Rittman[79] passes cracked residue through a pipe coil to produce an oil distillate and a so-called "coal" product.

Faragher, Morrell, and Essex[80] have found that the calorific value of cracked residuum is related to A.P.I. gravity by the following expression: B.Th.U. value=17,780+(54x° A.P.I. Gr.). They state that at 10° A.P.I. a cracked residuum has substantially the same fuel as a 10° A.P.I. gravity fuel oil, but as the A.P.I. gravity increases, the difference in B.Th.U. value of the two fuels enlarges until at 30° A.P.I. there is a difference between the fuel value of a flashed residuum made at two pressures and a normal residuum made at high pressures so long as the gravities are the same. The former usually possesses a lower A.P.I. gravity and hence a lower fuel value than the corresponding normal residuum.

They report no connection between the fuel value and such other characteristics of the fuel oil as volatility, source of the crude oil, coke-forming tendencies, B.S. content as determined by the benzol-centrifuge method, and carbon-hydrogen ratio. The main factors affecting the B.Th.U. value are moisture and sulphur.

PATENTS.

C. P. Dubbs (U.S.P. 1,727,308, Sept. 24, 1929) claims

> "A process for treating unvaporised residual oil accumulating during the cracking of hydrocarbon oil consisting in withdrawing the highly heated oil from the reacting zone of an oil cracking process, and in introducing the same to a coking still, in releasing the pressure on said oil in the coking still, and in applying heat to said oil to distil fractions thereof and to run the residue down to coke only by passing superheated steam through said oil."

Gustav Egloff (U.S.P. 1,683,767, Sept. 11, 1928) has devised

> "A process for treating residual hydrocarbon oil containing coke-like particles formed during a cracking reaction in suspension, to separate from the oil such coke-like particles as will not normally precipitate

[78] *Nat. Petr. News*, April 11, 1929, 68.
[79] *Nat. Petr. News*, Nov. 28, 1928, 33.
[80] *Ind. Eng. Chem.*, 1929, **21**, 933.

from the oil when maintained in a quiescent state, consisting in subjecting residual hydrocarbon oil withdrawn from a concurrent cracking operation to centrifugal action, causing the suspension to be broken and the coke-forming particles to be precipitated, in reducing the viscosity of the residual hydrocarbon oil before treatment by mixing with the same a hydrocarbon of lower boiling point, and in maintaining the temperature of the residual hydrocarbon oil undergoing treatment below 200° F."

GUSTAV EGLOFF (U.S.P. 1,688,861, October 23, 1928) covers

"A process for treating residuum which accumulates in the reaction zone of an oil-cracking apparatus during the conversion of hydrocarbon oil under heat and pressure which comprises withdrawing the residuum from such reaction zone, passing the same through a cooling zone, thence delivering the residuum to a tank filled to a substantial depth with liquid sulphur dioxide, agitating the residuum and the liquid sulphur dioxide in said tank, then discontinuing the agitation, permitting the residuum constituents and sulphur dioxide to stratify in upper and lower layers, separately drawing off the upper and lower strata and subjecting the separately withdrawn constituents to independent chemical treatments to obtain lubricating stock from the upper stratum and cylinder stock from the lower stratum."

GUSTAV EGLOFF and H. P. BENNER (U.S.P. 1,705,179, Mar. 12, 1929) treat oil-soaked carbon produced in an oil-cracking operation by

"Charging a still with a quantity of such oil-soaked carbon, subjecting said carbon to a heat treatment sufficient to distill off all the liquid constituents thereof by applying the heat centrally of said still to cause the heat to radiate through said oil-soaked carbon, and continuously agitating such carbon adjacent the walls of said still while undergoing said heat treatment."

L. C. HUFF (U.S.P. 1,683,826, Sept. 11, 1928) states

"An improved method for utilising the liquid residue from a hydrocarbon oil-cracking process, which comprises withdrawing the residual oil from a pressure cracking still, while at a temperature in excess of 400° F., lowering the pressure on the liquid residue, introducing the same to an enlarged zone, taking off vapours from said enlarged zone which have been evolved from the residual oil therein, in maintaining a body of the heated residual oil in said enlarged zone, continuously circulating the hot residual oil through a closed ring, including said enlarged zone, and supplying regulated quantities of the hot residual oil from said closed ring to selected furnaces positioned adjacent the ring, to constitute the fuel consumed therein."

J. C. MORRELL (U.S.P. 1,705,199, Mar. 12, 1929) treats residual oils resulting from cracking under heat and pressure by

"Withdrawing such residual oil from a reaction zone of a cracking process while in a highly heated condition, and in introducing to such highly heated residual oil sulphuric acid to act as a precipitating agent, in agitating the highly heated residual oil in the presence of the precipitating agent to cause the pitch-like and coke-forming particles in the residual oil to coalesce and be precipitated therefrom, the precipitating agent being taken up by the pitch-like and coke-forming particles to form a substantially solid mass."

J. C. Morrell (U.S.P. 1,733,620, Oct. 29, 1929) presents

"A process for stabilising the coke-forming particles of hydrocarbon residual oils resulting from an oil-cracking process comprising introducing to the residual oil an alkaline earth metal soap and in subjecting the residual oil to which the alkaline earth metal soap has been introduced to a homogenising treatment."

A. Oberle (U.S.P. 1,674,837, June 26, 1928) has devised

"A process for making carbonaceous fuel consisting in treating the residue resulting from the destructive distillation or cracking of petroleum hydro-carbons with steam under pressure, subsequently drying the treated residue by subjecting it to a reduced pressure, and then bringing a combustible gas in contact with the material to be absorbed thereby."

C. B. Watson (U.S.P. 1,673,854, June 19, 1928) claims

"The process of treating petroleum residue obtained from cracking and distillatory apparatus, which consists in circulating such residue through a conduit to a separating receptacle, in introducing an inert gas under pressure into said conduit so as to force said residue in an atomised finely divided form into said receptacle, in maintaining the temperature and turbulence of said residue within the receptacle by the introduction of an additional quantity of a heated inert gas into said receptacle, withdrawing the lighter fractions of said residue from adjacent the top of said receptacle and transmitting the same to separate condensing and collecting apparatus, in continuously circulating hot residual oil through a closed ring, including said enlarged zone, and in supplying regulated quantities of hot residual oil from said ring to a plurality of burners positioned adjacent said ring, to constitute the fuel consumed in said burners, the major portion of the residual oil circulated through said ring being permanently removed therefrom."

Arnold (E.P. 299,925, Dec. 31, 1928) presents a process in which

"Heavy hydrocarbon oils, such as cracking coal tar or pressure still tar, normally characterised by the formation of carbonaceous sediment on standing, are treated with 'acid oil' (prepared by diluting with water the acid sludge formed in treating petroleum oils with acid) to precipitate the sediment. An inert granular material, *e.g.*, coke, may be further added to aid filtering, and the oil is separated and may be used for fuel."

Standard Oil Development Co. (Goodwin R. T., Can. P. 282,000, July 24, 1928) claims a

"Process of treating a heavy hydrocarbon oil residue, derived from a cracking process and normally characterised by formation of carbonaceous sediment on standing, comprising bringing the said residue into contact with a small amount of acidic body in non-sludge forming concentration, whereby relatively rapid formation of sediment is obtained and separating the sediment."

3.—Vapour Phase Cracking

Wagner[81] outlines the progress which has been made in the Gyro process to reduce coke and gas formation. He states, "Coke

[81] *Nat. Petr. News*, Apr. 24, 1929, 40a; *Oil Gas J.*, Apr. 25, 1929, 46; *J. Inst. Petr. Techn.*, 1929, **15**, 484.

formation has been reduced to the point of being negligible by securing the best possible heat transfer, thus preventing local overheating, and by careful control of the time of cracking. Gas production is still twice as great as that from the liquid-phase cracking, but it is now controlled by very closely regulating the temperature of reaction, and the gas is made at the expense of the fuel oil, not of the gasoline."

Wagner states that the refining of vapour phase gasoline proved difficult because of its high degree of unsaturation. It was not a simple process to remove colouring matter and highly reactive olefines without at the same time reducing the anti-knock value of the motor fuel. He says, "Methods of removing colour-forming substances have now been worked out which involve not more than 5 per cent. of loss of the end point cracked distillate. A treatment is being applied which largely prevents the formation of gums on standing. The gasoline contains 40 to 45 per cent. of olefines and about the same percentage of aromatics; the balance is naphthenes, with only traces of paraffins.

In a later paper Wagner[82] gives results of small scale vapour phase cracking of a variety of charging stocks, including Cabin Creek, Seminole, Winkler, Mexican, and Ranger gas oil, topped Sweet Lake and Seminole crude and heavy Venezuela crude oil. Distillates ranging from 46·5° to 54·8° A. P. I. gravity with end points within the U.S. Motor gasoline limit were obtained in yields of 43 to 64 per cent.

Reid[83] also describes the operation of the Gyro process.

In the de Florez process[84] the heater is a circular pipe still, the tubes of which are arranged vertically around the inside wall and ends connected with return bends to make a continuous coil. The gas burner which heats the oil is supported at the top of the heater so that the flame shoots downwardly[85]. From Venezuela 18—20 gravity crude, an average yield of 30 per cent. pressure distillate of gasoline distillation range, 63 per cent. fuel oil, and 7 per cent. gas is reported. The gasoline is said to be of high anti-knock value. Pressure of 330 pounds on the inlet of the heater and 80 pounds on the bubble tower are used, with an average operating temperature of 1000° to 1100°F.

Auld[86] discusses the development of the vapour phase processes, mentioning those of Hall, Rittman, de Florez, Ramage and Gyro.

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[82] *Oil Gas J.*, Oct. 31, 1929, 46.
[83] *Ref. and Nat. Gas. Mfr.*, Jan., 1929, 68.
[84] Truesdell, *Nat. Petr. News*, May 1, 1929, 69.
[85] *Nat. Petr. News*, Apr. 24, 1929, 75.
[86] *Petr. Times*, 1929, 21, 99, 158.

Evans[87] describes the Knox process, in which oils are cracked at about 900—1000°F. by contact with heated gases. Some information is available regarding the operation of the vapour phase process of the Petroleum Conversion Corporation. In their operation oil vapours are cracked by admixture with hot recycled gas[88]. The proponents of this process claim freedom from carbon trouble and corrosion, low gas loss, and on gas oil charging stock a yield up to 80 per cent. of gasoline.[89]

Some experimentation with the Leamon vapour phase process has been carried out in California.[90]

UNITED STATES PATENTS.

A. P. Bjerregaard (U.S.P. 1,723,008, Aug. 6, 1929) claims

> "A process of treating petroleum hydrocarbons comprising vaporising said hydrocarbons, cracking said vapours at substantially atmospheric pressure, condensing out benzine from said vapours, and esterfying olefines formed in the gases by said cracking."

L. de Florez (U.S.P. 1,715,643, June 4, 1929) utilises as a part of cracking equipment

> "Vaporising apparatus for hydrocarbons comprising a source of heat, a heating chamber having vaporising members depending therein, said members in the hotter zone of the heating chamber having a reduced cross sectional area as compared with the cross sectional area of the depending members in the cooler zone of the heating chamber, and means for introducing the hydrocarbons to the vaporising members of larger area for passage thence to the vaporising members of reduced area."

L. de Florez (U.S.P. 1,674,390, June 19, 1928) cracks by a process

> "Which comprises continuously vaporising oil in a vaporising zone and heating the vapours to a cracking temperature in a cracking zone under pressure, progressively increasing the velocity of the hydrocarbons as they flow through said vaporising and cracking zones, discharging the vapours from the cracking zone and expanding them in such manner as to progressively decrease their velocity, and condensing the vapours remaining after expansion."

G. Egloff and H. P. Benner (U.S.P. 1,694,643, Dec. 11, 1928) include

> "In an apparatus for treating emulsified oil, the combination with a still, means for feeding a bulk supply of oil to the still, said still having a vapour space above the oil charge, of a burner extending lengthwise of said still and having gas discharge orifices throughout its length for applying the entire heat to the vapour space of the still, and means for agitating the liquid oil in the still below the surface thereof, said means comprising a rotary agitator extending through the still."

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[87] *Oil Gas J.*, July 12, 1928, 146.
[88] Stockman, *Oil Gas J.*, July 11, 1929, 138.
[89] *Oil Gas J.*, Sept. 19, 1929, 46.
[90] Truesdell, *Nat. Petr. News*, July 25, 1929, 19.

C. B. FORWARD (U.S.P. 1,698,811, Jan. 15, 1929) puts forward

"A process of refining oil, consisting in conveying a stream of oil through heating coils exposed to superheated steam and atomising the heated product together with a compressible fluid in a closed vessel, in forcing the volatilised and atomised product from the closed vessel through heating coils exposed to superheated steam of approximately 1000°F. or above, until high heated, and finally liquefying the highly volatilised product and separating the liquids so derived."

C. J. GREENSTREET (U.S.P. 1,718,913, June 25, 1929) covers

"A process of treating heavy hydrocarbon oils, which comprises mixing said oils with steam, passing the steam and oil under pressure, through a pipe extending back and forth through a furnace, burning a fuel in said furnace beneath said pipe throughout its length, passing the products of combustion of said fuel into contact with said heating coils, supplying air in regulated streams throughout the length of said fuel bed to regulate said combustion to maintain a substantially constant temperature of said products of combustion throughout the length of said heating coils at temperatures sufficient to produce cracking of the oils, and bringing the vapours from said coils directly into contact with a quantity of liquid sufficient to suddenly chill said products below a temperature at which further cracking of said oils will take place."

E. W. ISOM (U.S.P. 1,708,180, Apr. 9, 1929) presents

"A method of cracking hydrocarbon oils, comprising maintaining a body of oil at a cracking temperature by circulating oil from said body through heating tubes and back to the said body and heating the oil to a cracking temperature in said heating tubes, taking off vapours from said body of oil and subjecting them successively to a first and a second refluxing operation, returning reflux condensate from the first refluxing operation to said body of oil, forcing reflux condensate from the second refluxing operation once through a separate heating conduit and heating it therein to a cracking temperature, and discharging hot oil products from said heating conduit into said body of oil.

"For the production of gasoline or motor fuel components, to illustrate, the temperature of the oil body may be maintained in the neighbourhood of 750° to 800° F. and the temperature of the hot oil products as they are discharged from the heating conduit 23 may be maintained in the neighbourhood of 1000° to 1200° F."

E. W. ISOM (U.S.P. 1,711,351, Apr. 30, 1929) claims

"In cracking hydrocarbon oils for the production of lighter and lower boiling oils, the improvement which comprises heating the oil in the vapour phase to a high cracking temperature and, before condensation of the desired lighter and lower boiling oil, subjecting the vapours from the cracking operation to a fractionating operation, and introducing into direct contact with the vapours in the fractionating operation, as a cooling and condensing agent, an oil of boiling range corresponding to that of the desired lighter and lower boiling oil but substantially free from unsaturated components unstable at the temperatures prevailing in the fractionating operation."

W. J. KNOX (U.S.P. 1,715,239, May 28, 1929) covers

"The process of producing hydrocarbon compounds, which consists in feeding a liquid hydrocarbon into a chamber, heating said liquid hydrocarbon while in said chamber by contacting heated hydrogen containing gases therewith, subjecting the hydrocarbon coming into said chamber to a preliminary partial fractional distillation by thermally contacting the heated gases and vapours from said chamber therewith and passing the vapours and gases from said fractional distillation directly into said chamber."

H. L. PEEZER (U.S.P. 1,718,375, June 25, 1929) offers in cracking high sulphur crude oil

"The improvement which comprises subjecting oil to a vapour phase cracking operation and subjecting the vapour mixture from the said vapour phase cracking operation to a scrubbing operation for the separation of tar, mixing caustic alkali with the high-sulphur crude oil and introducing the caustic alkali-crude oil mixture into the vapours in the said scrubbing operation, subjecting the resulting vapour mixture escaping from the said scrubbing operation including the uncondensed components of the vapour mixture from the vapour phase cracking operation and the vaporised components of the crude oil introduced into the scrubbing operation to a refluxing operation, condensing in the said refluxing operation vapours heavier than suitable as components of the gasoline product including heavy components vaporised from the crude oil introduced into the scrubbing operation, supplying this reflux condensate from the said refluxing operation to the said vapour phase cracking operation, and discharging tar including tar components, separated from the vapour mixture from the vapour-phase cracking operation and from the crude oil introduced into the scrubbing operation and including any unconsumed caustic alkali and the solid or semi-solid reaction products of the caustic alkali from the said scrubbing operation without permitting this discharged tar to return to the said vapour-phase cracking operation."

J. B. WEAVER (U.S.P. 1,708,247, Apr. 9, 1929) utilises

"The combination with a pipe still in which the oil is subjected to heat while in the liquid phase, an expander in which the oil from the pipe still is permitted to expand into the vapour phase, a converter in which the vapours from the expander are subjected to a conversion action while in the vapour phase, a tar leg into which the vapours from the converter pass, a fractionating or scrubbing tower in which the uncondensed vapours pass from the tar leg, connections between said still and expander, expander and converter, converter and tar leg, tar leg and tower, and a lead from said tower and from said tar leg whereby the heavier products in both are conducted back to the pipe still."

ENGLISH PATENTS.

A. BALMER (E.P. 317,508, Oct. 9, 1929) reports that

"In a process for vapour phase cracking, petroleum, etc., is vaporised in a vaporiser preferably with the aid of steam or a neutral gas and passes to a reaction chamber where it is converted by the heat from carrier gases heated in a battery stove."

Compagnie Internationale pour la Fabrication des Essence et Petroles (E.P. 316,552, Sept. 25, 1929, not yet accepted) claims that

"In cracking oils by passage through a heated porous mass, which when covered with a carbon deposit can be reactivated by combustion in an air current, the impregnation of the porous material by the still liquid oil in the vicinity of the inlet is avoided by the use of a series of baffles."

I. G. Farbenindustrie A.G. (D.P. 294,557, Sept. 19, 1928) presents an apparatus in which

"Hydrocarbons are cracked by passing them in the state of vapour over a heating device arranged in a single plane and of relatively small dimensions in the direction of flow of the vapour. The heater may comprise a short length of piping arranged in the form of a grate or a rod, ribbon, or spiral of metal and may be exposed at intervals to a blast of air, hydrogen or of gases containing hydrogen to prevent deposition of carbon thereon. The apparatus comprises an enamelled vessel containing a heater comprising a number of nickel-chromium tubes maintained at 700° C. by passing therethrough a current of hot gases. Partially decomposed constituents are condensed in a condenser maintained at 100° C. and returned to the still, the light benzines being condensed in a condenser. The heating element may also consist of carbon, silicon-carbide, or graphite electrically heated and is protected from splashing by a baffle. The element may be cleaned mechanically."

W. G. Leamon (E.P. 317,868, Oct. 16, 1929) cracks mineral oils

"By vaporising in a coil of a pipe still, settling in a baffle chamber and a rotary separator, rapidly heating in a coil of the pipe still to a temperature above cracking temperature, not more than half the total cracking occurring at this stage and then passing the vapours to a cracking chamber wherein cracking is effected substantially wholly by the superheat of the vapours, after which the products pass to heat exchangers where the crude oil from a reservoir is preheated, thence to a dephlegmator and a condenser, condensates passing to reservoirs, some of the condensate from receiver being pumped into the dephlegmator by a pump. The cracking chamber may contain refractory porous adsorptive contact material which is inert to sulphur and nitrogen, *e.g.* amorphous and colloidal silica and silicerous compounds such as pumice, silica-gel, diatomaceous silica, etc."

J. Mercier (E.P. 302,899, Feb. 13, 1929, not yet accepted) presents an

"Apparatus for the depolymerisation of hydrocarbons comprising a boiler, series of tubular retorts, a regulating chamber and an expansion and cooling unit. The retorts are preferably of rectangular section and are filled with metallic scale or other suitable catalyst. They are built into a furnace and heated by hot gas flowing through the flue in counter current to the hydrocarbon vapours. The regulating chamber also contains catalyst, but is not heated. The expansion unit consists of a large chamber containing catalyst and provided in its upper part with water tubes to effect rapid colling of the vapour."

R. C. Osterstrom and C. R. Wagner (E.P. 317,507, Oct. 9, 1929) state that

"Hydrocarbon oils are cracked with substantial elimination of carbon deposition by reducing to the vapour phase at 650—850° F. by means of a pipe still, a steam jet, and an expansion chamber; separating

residual liquid and carbon in two stages by a condenser and a separator, substantially instantaneously raising the temperature to converting temperature in excess of about 1000° F. at a pressure not above 30 lbs. per sq. in. the conversion being completed in a period of time less than two seconds in the presence of a catalyser such as ferrous oxide, nickel oxide or other metal oxide capable of two or more stages of oxidation in a converter, the top pass of the cracking tube being arranged at the hottest part of the furnace; abruptly cooling to a temperature less than about 600° F. by means of a spray of oil at 200° F. or less, the temperature range of 600—1000° F. being substantially avoided throughout the operation."

C. J. PRATT (E.P. 293,829, Sept. 5, 1928, not yet accepted) produces cracking

"By first heating crude oils at low temperatures and then at higher temperatures under atmospheric pressure, and blending the vapours produced which are thus fractionated." A temperature of 1100° F. is mentioned.

TOCCO (E.P. 304,316, Mar. 13, 1929, not yet accepted) provides that

"The vapours produced by distilling oils or by the destructive distillation of coal, etc., are converted into hydrocarbon of low boiling point suitable for use in internal combustion engines by passing them after removal of sulphurous compounds over catalysts and fractionating the products by passage through a series of condensers the temperatures of which are controlled by molten metal or salt baths. The incondensible gases formed in the reaction are purified and after treatment by high tension discharges are passed over the surface of the condensate obtained from the first fractionation."

TRENT PROCESS CORPN. (E.P. 313,158, July 31, 1929, not yet accepted), covers a process in which

"Coal is carbonized in a vertical retort and the heat of the carbonized coal is utilised to crack oils. The coal is fed from an airtight hopper to the up-right retort heated by hot gases from burners circulating through tubes and compartments. The carbonized material falls into an oil seal and by its heat distills the oil and the vapours produced rising through the retort are cracked by contact with the hot descending coke."

H. WADE (E.P. 304,251, Mar. 13, 1929) arranges that

"In effecting catalytic reactions such as the cracking of hydrocarbon vapours, a finely-divided absorbent silica or like gel, preferably containing an active catalytic material such as iron oxide is mixed with the gas and carried through the reaction space in suspension, then separated therefrom, revivified, and then returned to the gas stream."

AUSTRALIAN PATENTS.

W. G. LEAMON (Australian P. 12,626, Dec. 31, 1928) reports that

"To convert heavy mineral oils into lower boiling products, vapours of the oil are caused to contact at cracking temperatures with refractory porous absorptive contact material, such as pumice, silica-gel, and the like, which is substantially inert towards sulphur and nitrogen under the conditions of operation, and then recovering liquid motor fuel from the resultant vapours.

"Mineral oil is pumped under pressure from a tank through heat interchangers and into the coil of a pipe still and is heated to a temperature of 360° to 425° C., and it then passes into a separator from which the vapours, substantially free of liquid, pass to a centrifugal separator, and thence at a high velocity through a heating coil, where they are brought to a temperature in the vicinity of 600° C., and they then pass into a cracking unit which contains a mass of porous absorptive contact material maintained at a temperature between 530° and 550° C. The main cracking occurs in the vessel (cracking unit) and the vapours then pass through the heat interchangers, a dephlegmator, and condenser to a receiver."

R. C. Osterstrom and C. R. Wagner (Australian P. 13,623, Dec. 31, 1928) disclose a process

"To prevent the formation of free carbon during the conversion of hydrocarbon oils, the latter are first heated to a vaporous state at a temperature of approximately 600° F., after which the temperature is substantially instantaneously elevated in excess of approximately 1000° F., and the vapours are maintained at the latter temperature for about two seconds and then substantially instantaneously cooled to a critical temperature less than approximately 600° F., and the subsequent treatment is carried out at temperatures not in excess of 600° F., whether or not the oil is in the liquid or vapour phase."

CANADIAN PATENTS.

L. de Florez (Can. P. 293,094, Sept. 17, 1929) discloses

"In an apparatus for cracking and distilling hydrocarbon oils, a distillation chamber, a fractionating column in vapour connection therewith, an outlet near the top of said column for withdrawing vapours of the lighter constituents, means for withdrawing intermediate constituents or cracking stock from an intermediate point in said column, a vessel for receiving said cracking stock, a heater adapted to raise the cracking stock to a cracking temperature, means for passing the previously distilled cracking stock without other components from said vessel through the heater, and means for passing the hot cracked products into said chamber including means for first mixing the cracked products with relatively cool fresh charge."

W. G. Leamon (Can. P. 280,295, May 22, 1928) describes an

"Apparatus for oil conversion comprising the combination, with a primary vaporiser, condenser means connected thereto, and a receiver to which condensate passes from said condenser means, of a second vaporiser, conduit means for conducting liquid to said second vaporiser from said receiver, a cracking chamber into which vapours pass from said second vaporiser, a plurality of fractionating devices, arranged in series, through which cracked vapours pass successively after leaving said cracking chamber for separation in liquid form of relatively heavy constituents therefrom, condenser means to which residual vapours pass from said fractionating devices, reflux conduit means for conducting to said primary vaporiser the heaviest portion of the constituents separated in said fractionating devices and for conducting to said receiver a less heavy portion of such separated constituents."

W. G. LEAMON (Can. P. 289,530, May 7, 1929) outlines a

"Process of oil conversion which comprises heat treating a mineral oil to obtain therefrom hot vapours substantially free from tarry constituents, passing said hot vapours through a mass of porous contact material substantially inert to sulphur, nitrogen and carbon under the conditions of operation, in such quantity and at such temperature that said mass of contact material is maintained by the passage of the hot vapours at cracking or converting temperatures not higher than about 600° C., and treating the resultant vapours to separate a motor fuel condensate therefrom."

W. G. LEAMON (Can. P. 290,510, June 18, 1929) claims

"The process of treating oil to obtain lighter products therefrom which comprises heating a body of oil to distil vapours therefrom, fractionating the distillate and returning the higher boiling portion thereof to said body of oil for further heating, and cracking a lower boiling portion of said distillate in vapour phase and in contact with a mass of contact material heated to a decomposing temperature, said contact material being substantially inert toward sulphur, nitrogen and carbon under the conditions of operation."

R. C. OSTERSTROM and C. R. WAGNER (Can. P. 291,984, Aug. 6, 1929) disclose a

"Process of converting hydrocarbon oil which comprises heating the oil to temperatures not in excess of 800° F., to change the oil from liquid to vapour form, then while the oil is in the vapour phase abruptly and substantially instantaneously raising the temperature of the vapours to converting temperatures in excess of approximately 1000° F., and then permitting the conversion reaction to occur in the presence of the last-named temperature, the oil vapours while undergoing said temperatures being maintained at pressures not in excess of substantially 30 pounds per square inch."

J. B. WEAVER (Can. P. 291,983, Aug. 6, 1929) offers

"In an apparatus for cracking hydrocarbon oil in the vapour phase, the combination with a pipe still, means for passing oil through said pipe still and therein subjecting the oil to temperatures sufficiently high to effect vaporisation of a portion thereof without substantially cracking the same, an expander arranged to receive the entire body of the oil released from said pipe still and serving to separate the liquid and vaporous fractions of the oil discharged from said still, separate outlets for removing from said expander the liquid and vaporous fractions of the oil, a converter through which the vaporised fractions of the oil alone are passed, means for heating the oil vapours passing through said converter to a temperature in excess of 1000° F., a cooler situated directly at the outlet of said converter, means disposed immediately adjacent to the position of entry of the vapours for introducing liquid oil into said cooler and into intimate contact with the oil vapours discharged from said converter to effect quick reduction in the temperature of said vapours to a temperature precluding the liberation of free carbon, means for passing the liquid oil from said cooler to said pipe still, and means for fractionating and condensing the vapours released from said cooler."

H. T. WRIGHT and F. ESLING (Can. P. 281,879, July 24, 1928) devise

"An oil conversion process of the vapour phase type, wherein oil is vaporised in one zone and the vapour produced is transferred to and cracked in another zone, which process consists in preheating the oil under pressure prior to vaporisation, substantially to the temperature of the vaporising step under conditions of temperature and pressure which are substantially inhibitive of vaporisation and cracking, separating a portion of the preheated oil by vaporisation under conditions of temperature and pressure which are substantially inhibitive of cracking, thereafter cracking the separated vapour by superheating it gradually, expanding the cracked vapour into a region of relatively reduced pressure and thereby condensing its heavier fractions, subjecting the condensate of this step to subsequent conversion treatment, and fractionally condensing the uncondensed portion of the expanded cracked vapour by subjecting said portion to cooling."

FRENCH PATENTS.

I. W. HENRY (F. P. 654,622, May 21, 1928) claims that

"Vapour phase cracking of liquid and solid hydrocarbons is effected by dissociating them into gases containing hydrogen and carbon, ionising the carbon molecules in oil vapours and combining them with hydrogen produced by the dissociation of superheated steam. The process is carried out in a chamber filled with electrically conductive blocks of carbon or graphite which form a short circuit, and by inducing, by a coil surrounding the chamber, and oscillating spark-free electro-magnetic field of high frequency. The treatment of the cracked products is repeated in another smaller reaction chamber. A catalyst may be employed."

R. C. OSTERSTROM and C. R. WAGNER (F. P. 654,282, May 15, 1928)

"State that in cracking hydrocarbon oils the vapours are raised almost instantaneously to a conversion temperature about 535° C. The oil is first heated to 315°—420° C. and then suddenly to 535°, the conversion being completed in less than 2 seconds above this temperature and at a pressure of 2 kilograms per square centimeter. Steam is added to the vapour before heating to 535°, and a metal oxide having two stages of oxidation, such as FeO, is used as catalyst."

4. CRACKING WITH CATALYSTS OR CHEMICAL REAGENTS (EXCLUDING HYDROGENATION).

(a) *Aluminium Chloride.*

Waterman and Van Soest[21] heated Rangoon paraffin wax in a distillation flask with aluminium chloride. Gasoline began to form at 180° C., and a yield of between 18 to 23 per cent. was obtained. Fifty to sixty-two per cent. of the original material was recovered unchanged.

[21] *J. Inst. Petr. Techn.*, 1928, **14**, 756.

Schneider[92] studied the action of aluminium chloride on hexane and isohexane and states :—

"The action of aluminium chloride on the two paraffins is similar to its action on aromatic hydrocarbons. There is a breaking down, followed by a building up of the carbon chain. The gaseous decomposition products consist of butane, a little propane, pentane and unchanged hexane, but no methane. The liquid residues consist of hydrocarbons boiling higher than the original material. Unsaturated hydrocarbons were held back in the aluminium chloride sludge, and were obtained by leaching the sludge with ice water.

"In cracking saturated hydrocarbons, the aluminium chloride does not act as a true catalyst because it can decompose only a definite quantity of hydrocarbon. In breaking C–C or C–H bonds unsaturated compounds are formed which combine with aluminium chloride so that further cracking is prevented. The hydrogen is not liberated as such, but reduces some material present."

McAfee[93] describes the improved method of producing aluminium chloride of the Gulf Refining Company, which has made possible extension in the use of this reagent. Bauxite is calcined, briquetted with coal, carbonised, and chlorinated at 1600° F.

PATENTS.

H. Blumenberg, Jr. (U.S.P. 1,673,491, June 12, 1928) claims

"A process of cracking crude mineral oils comprising adding aluminium chloro sulphate to crude mineral oil, heating the oil to cracking temperature, distilling the oil, and condensing the distillate.

"The mineral oil is heated to temperatures used in the cracking process varying from 70° C. to 300° C., or even higher, and any suitable or preferred pressure as is now the common practice may be used, though most mineral oils when treated with aluminium chloro sulphate may be cracked at normal pressure."

W. F. Downs (U.S.P. 1,716,372, June 11, 1929) presents

"An apparatus for treatment of mineral oils, including a still adapted to receive the oil to be treated and aluminium chloride, means for heating said still to a temperature at which vapours are evolved, means closely adjacent to the bottom of said still for causing an upward circulation of solid matters settling to the bottom, and separate beater mechanism above said upward circulating means for breaking up said solid matter, a condenser having a filter bed therein, means for conducting vapours from said still to said filter bed, means for maintaining the temperature of the vapours above the volatilising point of aluminium chloride while passing from the still to the filter bed, and means for maintaining the temperature of the filter bed below the volatilising point of aluminium chloride."

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[92] *M.I.T. Publications Abstr.*, Jan., 1928, 72.
[93] *Natl. Petr. News*, July 17, 1929, 83.

L. Edeleanu (U.S.P. 1,671,517, May 29, 1928) covers

"The process for preparing an agent for converting mineral oils into light oils of lower boiling point which consists in mixing mineral oils with liquefied sulphur dioxide, separating the undissolved constituents of the said mineral oils from the constituents dissolved in liquefied sulphur dioxide, dissolving aluminium chloride in the said undissolved constituents of mineral oils at temperatures below those at which the mineral oils are converted into lighter hydrocarbons and separating the hydrocarbons from the formed oil."

G. Egloff (U.S.P. 1,692,203, Nov. 20, 1928) outlines

"A process of treating hydrocarbon oil comprising heating said oil maintained in a substantial liquid body in the presence of aluminium chloride, maintaining a temperature within said body above the melting point of the aluminium chloride, and sufficient to vaporise portions of the oil, withdrawing the unvaporised oil and aluminium chloride from the lower part of the liquid body and re-introducing same to the upper part of the liquid body, and continuing such circulation during the treatment, the oil and chloride being returned to the liquid body in an atomised condition."

G. Egloff and J. C. Morrell (U.S.P. 1,705,180, March 12, 1929) disclose

"A process for the conversion of hydrocarbon oil, consisting in initially raising the oil to a cracking temperature, in injecting into the oil, while at a cracking temperature, regulated quantities of hydrogen chloride, in passing the commingled heated oil and hydrogen chloride into an enlarged zone containing a quantity of disintegrated aluminium, in taking off vapours from said enlarged zone for condensation and collection, and in maintaining a superatmospheric vapour pressure on the oil undergoing conversion in the process."

I. G. Farbenindustrie A.-G. (E.P. 306,437, April 17, 1929) states that

"Hydrocarbons which are soluble in liquid sulphur dioxide, and are liquid at ordinary temperatures, may be converted into hydrocarbons of a low boiling-point range, up to 200° C., and with a high content of benzene and toluene, by treatment with anhydrous aluminium chloride. The process is carried out at temperatures above 100° C., preferably while stirring, and while passing nitrogen or other inert gases, hydrogen chloride, etc., through the mixture, at ordinary or elevated pressure. Aluminium metal or a mixture of it with anhydrous aluminium chloride may be used as catalyst while simultaneously acting on the hydrocarbons with dry hydrogen chloride."

G. L. Prichard and H. Henderson (U.S.P. 1,672,339, June 6, 1928) have devised

"The process of converting higher boiling oils into lower boiling oils which comprises distilling the higher boiling oils in the presence of anhydrous aluminium chloride, withdrawing from the mixture used aluminium chloride in the form remaining after its activity is partially spent, heating the withdrawn aluminium chloride in such form and passing the volatile products of such heating to the vapour space above the mixture of aluminium chloride and higher boiling oil undergoing conversion."

G. D. WHITE (U.S.P. 1,726,280, Aug. 27, 1929) claims an

"Apparatus for treating hydrocarbons comprising a still, a mixing chamber for aluminium chloride and oil connected with the still, a pair of recovery stills adapted to receive sludge from the main still and connected to discharge aluminium chloride vapours into the main still."

J. C. CLANCY (Can. P. 289,407, May 7, 1929) claims

"In a process of converting higher boiling oils into lower boiling oils, the combination of steps which comprise introducing a stream of a mixture of such higher boiling oils and aluminium chloride into the upper end of a sealed retort having a portion thereof maintained at a temperature to effect an oil cracking reaction therein, delivering into contact with the said oil mixture a stream of a metal chloride which is capable of holding in suspension a portion at least of the carbon separated out in the reaction, the said metal chloride being in a molten condition, and comprising zinc chloride and an alkali metal chloride, preventing the accumulation of carbon deposits in the retort by allowing said molten chloride containing such suspended carbon and the unvaporised oil, carrying its quota of separated carbon in suspension to discharge from the retort and collecting the evolved vapours of lower boiling oils and aluminium chloride from the retort."

(*b*) *Other Catalytic Conversions.*

Darmois[94] cracked kerosine and other petroleum oils by passing through a heated glass tube in the bottom of which was placed a catalyst. An initial decomposition with iron and nickel began at 400° C., with copper at 450° C., and heating silver to about 500° C. As the temperature rose the amount of gasoline obtained increased to a maximum and then decreased, while the amount of gas increased continuously. In general, the gasoline and gas obtained at low temperatures contained ethylene and hydrocarbons containing three or more double bonds, but no acetylene. As the decomposition temperatures increased, the proportion of ethylene among the unsaturates was enhanced, and the gasoline contained a larger proportion of aromatics. Test on a gasoline of known composition showed that the aromatic hydrocarbons were stable under the condition of the experiment while the naphthene hydrocarbons produced chiefly ethylene.

Koudelak[95] studied the effect of numerous catalysts on the cracking of paraffinic oils of Czecho-Slovakian origin. The experiments were carried out at atmospheric pressure and temperatures from 410° to 500° C. Among the most satisfactory catalysts were oxides of nickel and tin and a composition of a silver slag mixed with clay. The yields of gasoline ranged from 5 to 40 per cent. They were refined by the Gray process and remained water white even after four years.

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[94] *Chimie and Industrie Special No.* 252-6 (Feb., 1929).
[95] *Paliva a topeni*, 1929, **10**, 117, 137, 145. *Chem. Abstr.*, 1929, **23**, 2811.

Goldthorp,[96] in continuation of the work of Gault, investigated the cracking of hexadecane and hexadecene in the presence of nickel and iron catalysts.

UNITED STATES PATENTS.

H. Blumenberg, Jr. (U.S.P. 1,713,252, May 14, 1929), covers

"The process of treating mineral oils and their products comprising adding a metal hypochlorite in dry form thereto and subjecting the same to a cracking temperature to increase the lighter fractions by splitting up the heavier molecules of the mineral oil or product."

J. C. Clancy (U.S.P. 1,721,728, July 23, 1929) claims

"The process of cracking hydrocarbons, which comprises subjecting a hydrocarbon to be treated to the action of a reagent comprising a molten mixture of alkali metal cyanide and alkali metal formate, said reagent being maintained at a cracking temperature."

G. Egloff (U.S.P. 1,722,042, July 23, 1929) presents

"A process of cracking petroleum oil, consisting in passing oil in a continuously advancing stream through a cracking zone where said oil is subjected to a cracking temperature while maintained under a super-atmospheric pressure, in introducing the oil to an enlarged chamber where vaporisation thereof occurs, in reducing the pressure in said chamber below the pressure maintained on the oil in the stream, but above atmospheric, in causing the vapours from the oil in the chamber to pass through a catalytic bed comprising a relatively thin layer of a metallic oxide supported in the vapour space of said chamber, in discharging vapours from the chamber, and in condensing said vapours for collection as pressure distillate."

E. Erlenback (U.S.P. 1,671,573, May 29, 1928) devises a

"Process for the cracking of heavy hydrocarbons, mineral oils, oil residues, tars and the like in a still having a body of catalytic material extending entirely across the still and dividing the liquid body, which comprises maintaining a liquid body in the still at a cracking temperature, withdrawing the liquid from below the catalytic body and returning it above the catalytic body whereby all of the liquid is circulated through the catalytic body."

E. T. Hessle (U.S.P. 1,696,913, June 1, 1929) has invented

"A process of converting hydrocarbon oils into lower boiling products which includes the step of directing a hydrocarbon oil against a counter-current stream of a gas under sufficient pressure to form a true fog of oil and then passing said fog through a molten decomposition catalyst consisting of an alloy of tin and antimony containing less than 10 per cent. antimony, whereby decomposition of the oil takes place in the liquid phase, the resulting lower boiling products being released from said catalyst in vapour form."

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[96] *Ann. combustibles liquides*, Mar.-Apr., 1928, 219.

E. T. Hessle (U.S.P. 1,702,540, Feb. 19, 1929) covers

"A process of converting hydrocarbon oils into lower boiling products, which includes directing the oil against a counter current stream of a hydrocarbon vapour under sufficient pressure to form a true fog of highly dispersed liquid oil suspended in said vapour, and passing said fog through a decomposition catalyst whereby decomposition of the oil and vapour takes place to form lower boiling products."

H. J. Jansen (U.S.P. 1,672,459, June 5, 1928) claims

"A process for cracking hydrocarbons, comprising the steps of passing the hydrocarbons in an extended and substantially horizontal path through a molten mass composed of lead with a top layer of zinc chloride which is heated to cracking temperature and which has only a small free surface; and withdrawing the hydrocarbon vapours escaping at such surface, and the carbon carried in suspension therein, so as to avoid the formation of a residue on said surface."

J. R. Mardick (U.S.P. 1,706,629, March 26, 1929) describes

"The method of cracking oil which comprises heating a high boiling point oil, and subjecting such oil to the action of previously electrically activated chlorine in the absence of sufficient moisture to materially interfere with such cracking operation, and then collecting the relatively low boiling point distillates obtained by such treatment."

T. Midgley, Jr. (U.S.P. 1,721,523, July 23, 1929), has devised

"The process of treating a hydrocarbon oil which comprises vaporising the hydrocarbon oil and cracking the vaporised oil by contact with a catalyst of the selenium type."

J. Perl (U.S.P. 1,689,362, Oct. 30, 1928) arranges

"In a pressure still for cracking hydrocarbon oils, a tubular heater, connections adapted for circulating and recirculating a liquid body of oil in the still therethrough, and means for circulating heating gases externally about the tubular elements of the heater, the internal surface of the tubular heater elements having a tin-containing coating thereon."

J. Perl (U.S.P. 1,689,363, Oct. 30, 1928) places

"In a pressure still for cracking hydrocarbon oils, a tubular heater, means for circulating heating gases externally about the tubular elements of the heater and means for circulating the oil therethrough, the internal surface of the tubular heater elements having an iron sulphide coating thereon."

Schmidt, Grosskinsky, and Niemann (U.S.P. 1,732,381, Oct. 22, 1929) claim

"The process of splitting hydrocarbons having a higher molecular weight than the desired products to olefines and diolefines which consists in bringing the hydrocarbon vapours into contact, at temperatures above 500°C., with a contact mass comprising a difficulty reducible metal oxide."

Sigbert Seelig (U.S.P. 1,732,664, Oct. 22, 1929) presents

"In an apparatus for cracking oils and the like, a reaction vessel adapted to be externally heated and to contain a charge of molten metal, a continuous spiral tube annularly spaced from the inner walls

of said tube being adapted to contain a fluid circulating therethrough to retard the flow of heat from said walls to the interior of the vessel, and means to conduct oil to be treated into said vessel."

C. P. TOLMAN (U.S.P. 1,733,143, Oct. 29, 1929) covers in cracking

"The steps which consist in evolving mercury vapour from mercury liquid under conditions producing substantially saturated vapour having a temperature not materially in excess of the desired conversion temperature, introducing said evolved vapour into physical contact with said hydrocarbon compounds in a reaction zone and so proportioning said mercury vapour to said hydrocarbon compounds in said reaction zone as to constitute said mercury vapour the sole source of heat bringing about said conversion reaction, whereby said mercury vapour furnishes said heat at the substantially uniform temperature of its condensation, withdrawing the converted products from said reaction zone and recovering from said products hydrocarbon compounds of lower molecular weight."

AUSTRALIAN PATENTS.

K. GEISSEN (Australian P. 7,961, July 10, 1928) claims

"A method of producing or converting oils, in which solid, liquid, or gaseous fuels or tar or the like, mixed together or with other solid, liquid, or gaseous substances, in a fine state of subdivision, are subjected to the action of a high voltage electric current. Catalysts in the form of powder, mist, or gas are added, or the electrodes used are made of substances that act completely or partially as catalysts, or they are covered or incorporated with such substances.

"The raw material may be treated under superatmospheric pressure and may be heated before or after entering the reaction chamber, and the treatment may be carried out in an atmosphere of hydrogen."

A. S. KNOWLES and C. W. ANDREWS (Australian P. 16,305, July 9, 1929) state that

"To dehydrate, distil, and crack tars, pitches, and the like, which are liquid at normal temperatures or are capable of liquefaction by heating, they are passed in thin films in a closed, heated chamber, whereby they are partially volatilised, and the liquid residue is deposited on the floor of the chamber and there coked.

"The hydrocarbon to be treated flows from a pipe into a pipe which distributes it on to loose coke in a basket within a heating chamber. The hydrocarbon flows over the coke and is distributed on to a rotating corrugated drum, over which it flows in a thin film and is partially volatilised before it drips on to the refractory chamber floor and there spreads out, when it is rapidly coked, and the ascending heated volatiles pass up around the drum and around and through the basket to the vapour outlet, while the coke is periodically removed through doors. The chamber floor is composed of bricks containing in excess of 60 per cent. of aluminium oxide."

E. SCHULTZ and E. L. SCHULTZ (Australian P. 9,692, Jan. 15, 1929) claim

"To recover a high percentage of light oil from organic materials, such as crude oil, shale, and the like, the raw material, as crude oil, is vaporised in a still and the vapours are passed into a converter

constructed of zinc nickel and lead, or sherardised steel, and containing lime and zinc chloride or zinc oxide, which are agitated by paddles, and cause the gases to react under pressure which is maintained therein and gradually increased, as the temperatures in the still and converter are both gradually increased, so that after the gases have been condensed an odourless high-grade light oil is produced. A pressure of from 2 to 10 lbs. per square inch is maintained in the converter by means of an expansion valve of the needle type, which is located in the vapour outlet pipe between the converter and the condenser.

"In a modified form of apparatus, a dephlegmator is located between the converter and the condenser."

W. H. SMITH (Australian P. 12,660, April 16, 1929) discloses a process

"To simultaneously reduce iron ore and convert hydrocarbons, iron ore, together with other catalytic agents such as nickel, chromium, or reduced sponge iron, is fed from hoppers into a retort which is divided up into a series of smaller retorts by means of heating units. The latter being hollow in the upper portion to receive electrical resistance elements. Hydrocarbons such as mineral oil are introduced into the retort through valves, and may be fed into the bottom part of the heating units, and will then be partially refined, and the lighter liquids and gases will pass upwardly and out into the retort through the valves and the heavier hydrocarbons left behind may be drained off. The reduced ore in the retort will be cooled by the incoming oil as it passes upwards to the valves, and enters the retort just below the reducing zone, and the gases passing upwardly react with the ore to effect reduction."

CANADIAN PATENTS.

W. T. DONALDSON (Can. P. 293,194, Sept. 17, 1929) describes a

"Method of producing lower boiling hydrocarbons from higher boiling ones that comprises heating hydrocarbon oil to vaporising temperatures to thereby evolve vapours, forming from the vapours a lighter and a heavier condensate the former of which comprises essentially constituents the critical temperature of which is at or below their cracking temperature, and the latter of which is substantially free from such constituents, subjecting the heavier condensate to thermal decomposition to produce lower boiling oil, and treating the lighter condensate with a metal halide to effect the formation of lower boiling products."

P. G. GREENE (Can. P. 289,745, May 21, 1929) offers

"A process for converting heavy hydrocarbons, particularly those distilled from solid fuel, into light and stable hydrocarbons, comprising treating the hydrocarbons to convert them into form of vapours by passing them over a carbonaceous catalyst which promotes the operation of cracking and at the same time opposes the deposit of carbon."

C. N. HAYDEN (Can. P. 284,942, Nov. 20, 1928) reports a

"Continuous self-sustaining process of destructively distilling and gasifying hydrocarbon materials which comprises continually introducing the material to be treated into the zone of reaction, charged upon pieces of inert refractory material as a carrier, passing the charged carrier material progressively through the sphere of reaction, and withdrawing

it, and subjecting the advancing material to a limited counterflow combustion agent, so as to create in the sphere of reaction a region of cracking of the hydrocarbon material under treatment, and a subsequent region of combustion of the coke from such cracking, thereby furnishing heat for the cracking and restoring the carrier material to clean, uncharged condition."

I. G. FARBENINDUSTRIE A.-G. (Can. P. 285,916 Dec. 25 1928) has devised a

"Process of producing hydrocarbons of low boiling point which consists in acting on hydrocarbons of high boiling point with hydrochloric acid gas at temperatures above 100° C. in the presence of aluminium activated by a solution of a salt of such metals as possess a higher potential value than aluminium."

F. LAMPLOUGH (Can. P. 283,681, Oct. 2, 1928) claims

"A process for the conversion of hydrocarbon oils to oils of lower boiling point, which comprises admixing the oil with a normally solid cyclic hydrocarbon such as naphthalene, and subjecting such a mixture to a temperature lying between 300° C. and 400° C. while under a pressure higher than the vapour pressure of the oil, thereafter cooling the oil to such a temperature that the heavier portion of the hydrocarbons will remain in a liquid state but the lighter portion partly or wholly formed in the process will be vaporised upon release of the pressure, and releasing the pressure and separating the lighter hydrocarbons."

ENGLISH PATENTS.

BATAAFSCHE PET. MAATSCHAPPIJ (E.P. 302,349, Feb. 6, 1929, not yet accepted) states

"Hydrocarbons are cracked in the presence of halogens or halogen compounds, including iodine and its compounds when gaseous hydrocarbons are treated, but excluding such bodies when liquid hydrocarbons are decomposed. Compounds of halogens containing hydrogen, sulphur, phosphorus and oxygen may be used as well as the elementary halogens. Activators such as copper, iron, or their salts, oxygen, sulphur, &c., may also be added."

BIANCHI AND GUARDABASSI (E.P. 312, 399, July 17, 1929) present the improvement

"In apparatus of the kind described in Specifications 277,404 and 278,041 in which oils are distilled, cracked or hydrogenated by passage through heated troughs provided with agitators mounted on the shafts, shafts are made hollow and are connected together to form a continuous coil through which the liquid to be heated is forced and thus preheated. The liquid emerges from the coil through a nozzle, and is sprayed on to a reticulated screen from which depend chains preferably coated with catalytic material."

J. C. CLANCY (E.P. 304,421, Mar. 13, 1929) states that

"Low boiling point oils are obtained by distilling oils of higher boiling point in contact with an alkali metal cyanide, *e.g.*, molten sodium cyanide. Hydrogenation of the vapours produced is effected by the ammonia formed during the reaction, and also by ammonia and other hydrogenating gases admitted from exterior sources. Metallic catalysts, *e.g.*, iron, nickel, copper, may be added to the reacting material. . . ."

F. B. Dehn (E.P. 289,556, June 20, 1928) finds that

"The cracking of hydrocarbon oils such as black asphalt, crude oil, kerosine, gas oil, lubricating oil, tar residuum, etc., is promoted by adding before or during the heat treatment a colloidal substance such as bentonite, hydrated lime, etc. The forms of bentonite which form jellies on admixture with water or alcohol are suitable. The colloidal substance may, before addition to the oil, be dispersed in or formed into a gel with water, alcohol or a portion of the oil. The addition of the colloidal substances to the oil renders it less viscous, and results in a distillation residue resembling natural asphalt in its content of mineral."

Electro Metallurgical Co. (E.P. 298,556, Dec. 5, 1928, not yet accepted) cracks oil

"In apparatus made or lined with an alloy containing chromium 15—40 per cent., nickel 2—15 per cent., silicon 0·7—3 per cent., manganese 0·7–3 per cent., the remainder consisting mainly of iron and containing not more than 1 per cent. of carbon."

I. G. Farbenindustrie A.-G. (E.P. 293,887, Sept. 5, 1928) finds that

"A product consisting chiefly of aromatic hydrocarbons is obtained by heating with a dehydrogenating catalyst the liquid hydrocarbons obtained by destructive hydrogenation of carbonaceous materials or the distillation or extraction products of these hydrocarbons. Specially effective catalysts are oxides of metals of the 6th group with or without oxides of elements of the 3rd and 4th groups. Other catalysts such as silver, copper, chromium and nickel alloys, aluminium, iron sponge, porous carbon, zinc sulphide, alumina, pumice, cadmium sulphide and palladium may, however, be used."

I. G. Farbenindustrie A.-G. (E.P. 296,694, Oct. 31, 1928) coats the hot parts of apparatus in which hydrocarbons are treated at high temperature

"With lustrous carbon to prevent deposition of soot. Lustrous carbon (Glanzkohle) is a form of carbon deposited from hydrocarbons at temperatures above 650° C."

I. G. Farbenindustrie A.-G. (E.P. 296,752, Oct. 31, 1928) treats the hot parts of apparatus in which hydrocarbons are treated at high temperature.

"With metalloids, namely boron, arsenic, antimony, bismuth, phosphorus, selenium, or compounds of any of these, or with silicon, to prevent deposition of carbon. Mere traces of the additions are sufficient; they may be introduced by treating the apparatus with solutions or vapours containing the metalloid compounds, or by adding metalloid compounds to the hydrocarbons under treatment."

I. G. Farbenindustrie A.-G. (E.P. 297,398, Nov. 14, 1928) converts mineral or artificially prepared hydrocarbons containing more than four carbon atoms in the molecule

"Into olefines and diolefines containing a smaller number of carbon atoms in the molecule than the initial materials by bringing their vapours, at normal or reduced pressure and at a temperature of at least 600° C., into contact with catalysts consisting wholly or for the most part of difficulty reducible metallic oxides or mixtures or compounds thereof, along or in conjunction with supports."

I. G. Farbenindustrie A.-G. (E.P. 303,761, Mar. 6. 1929) produces hydrocarbons of low boiling point

"From hydrocarbons of high boiling point by treatment with a gaseous hydrogen halide at temperatures above 100° C. with or without pressure in presence of activated metals or alloys, such as aluminium, copper, lead, magnesium, iron, cobalt, chromium and the like, and their alloys."

I. G. Farbenindustrie A. G. (E.P. 303,998. March 6. 1929) obtains olefines and diolefines

"By catalytic treatment in a vaporous state of paraffins, olefines or mixtures thereof, which may be cyclic, at temperatures between 500—800° C., using as catalyst lustrous carbon (Glanzkohle) which is deposited from hydrocarbons at temperatures above 650° C. It may advantageously be employed on carriers, such as difficult reducible metal oxides and compounds or mixtures thereof."

I. G. Farbenindustrie A.-G. (E.P. 307,945, May 8, 1929) states that

"Diolefines are obtained by heating aliphatic or cyclic paraffins or olefines obtained from mineral or artificial sources with $\frac{1}{3}$ volume or more of steam in the presence of catalysts."

I. G. Farbenindustrie A.-G. (E.P. 309,227, May 29, 1929) cracks liquid carbonaceous materials, *e.g.*, tars, oils, etc.

"In the presence of organic substances containing the radical of a mineral acid in the molecule which reduce the surface tension of water, *e.g.*, aromatic and aliphatic sulphonic acids, sulphonic acids of aromatic and hydro-aromatic hydrocarbons sulphonated in the nucleus, and containing at least one alkyl group in the nucleus. Specific examples are benzene sulphonic acid, phenyl borate, the residue obtained by evaporation of sulphite cellulose waste liquor. Substances having a catalytic action, *e.g.*, alkalies, magnesia, or zinc oxide may also be added."

I. G. Farbenindustrie A. G. (E.P. 315,991, Sept. 11, 1929) produces low boiling point hydrocarbons

"From mineral oils, tars, products of the hydrogenation, distillation or conversion of coals, tars, oils and the like into low boiling products, by acting upon the said materials at an elevated temperature and in the presence, or not, of gases or vapours with aldehydes or ketones, which latter contain more than three carbon atoms in the molecule. Metals, oxides or salts may be employed in addition to, or in combination with, the aldehydes and ketones."

I. G. Farbenindustrie A. G. (E.P. 316,037, Sept. 25, 1929) states that

"Hydrocarbons of low molecular weight are obtained by splitting hydrocarbons of high molecular weight such as mineral or tar oils, in the presence of a catalyst consisting of or containing a salt of metaphosphoric acid, especially a heavy-metal salt, and in particular the metaphosphates of metals of the 6th group of the periodic system, *e.g.*, uranyl and chromium metaphosphates. The process may be carried out in the liquid or gaseous phase, but preferably by passing vaporised hydrocarbons over the catalyst in association with inert gases, such as nitrogen and carbon dioxide, at temperatures from 400—800° C., and, if desirable, under pressures up to 50 atmospheres. The catalyst may be contained on a carrier, *e.g.*, pumice, silica gel, etc. In addition to hydrocarbons of low boiling point, unsaturated hydrocarbons, *e.g.*, ethylene, propylene and butylene, are obtained."

S. Seelig (E.P. 296,000, Oct. 17, 1928, not yet accepted) distils and cracks oils which contain impurities such as resins, benzene, etc., by passing them continuously through a molten metal bath, and prevents "clogging of the reaction vessel, *i.e.*, by pumping the oils from stock through an asphalt separator and then distilling off the benzene under slightly increased or diminished pressure before passing the oils to the reaction vessel."

Smith (E.P. 288,193, May 31, 1928) cracks oils and simultaneously reduces ores, especially iron ore,

"by passing the oils through a series of heated closed chambers or retorts through which a stream of ore is continuously fed. The retorts are preferably heated by electric resistances to control the temperatures accurately. The iron ore acts as a catalytic agent but the retort walls may also be lined with catalysts, *e.g.*, chromium, nickel, magnetite, reduced iron sponge, may be mixed with the ore."

Soc. Anon. Le Carbone (E.P. 290,060, June 27, 1928) states that

"low boiling-point oils are obtained from vegetable and mineral oils by passing them through heated activated porous carbon in block form. Gas oil containing 75 per cent. distilling over 250° C. was passed through activated black carbon heated to 350° C. and a product was obtained comprising 35 per cent. combustible gases and a liquid residue containing 6 per cent. distilling up to 110°, 6 per cent. from 110°—150°, 9 per cent. from 150°—200°, 20 per cent. from 200°—250° C."

Tolman (E.P. 299,957, Dec. 31, 1928) uses mercury vapour

"as the sole source of heat for bringing oil vapours to the cracking temperature. The mercury is vaporised in a boiler and passed through a superheater to a reaction chamber where it is intimately mixed with oil vapours supplied from an evaporator. The reaction products are withdrawn through a pipe to a condenser and separator, the mercury being returned to the boiler through a pipe while the light oils produced are separated in a receiver from any permanent gases."

Trent Process Corporation (E.P. 313,597, Aug. 8, 1929, not yet accepted) devises a process for reducing iron ores in which

"The ore mixed with carbonaceous material is heated in a furnace and the iron produced is deposited in oil which coats the iron and protects it from oxidation, the oil vapours rising in the furnaces and by contact with the hot reduced ore being cracked, the products of the cracking being removed from the furnace."

Van Peski (E.P. 315,193, Sept. 4, 1929) decomposes hydrocarbons

"into other hydrocarbons containing fewer carbon atoms, without the use of hydrogen or gases capable of yielding hydrogen, by treatment at high temperatures with one or more metallic carbides or with metals or metallic compounds which yield carbides under the conditions of the process. Complex carbides such as iron-tungsten carbide may be employed. In the examples (1) propane is passed at 600—800° C. over calcium carbide or molybdenum mixed with pumice, the products being ethylene and methane; (2) gas oil boiling at 220—340° C. is passed at 350—700° C. over calcium carbide, yielding a liquid condensate boiling at 60—180° C. and some gas containing unsaturated hydrocarbons."

GERMAN PATENT.

A. A. SEIGLE (D.R.P. 472,734, May 8, 1929) covers an installation for distillation and breakdown of mineral oils and similar hydrocarbon mixtures by a process in which the oils under approximately atmospheric pressure are led through one or more retorts, which form a coil, and in which they pass through catalysers.

NEW ZEALAND PATENTS.

(The quoted portions for New Zealand patents are from the Illustrated Official Journal.)

DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ (New Zealand P. 61,931, June 27, 1929) claims an invention

> ". . . characterised by the fact that hydrocarbons which are normally in the gaseous phase are split in the presence of halogens or halogen compounds (iodine or iodine compounds included), and that liquid hydrocarbons having high-boiling points are split in the presence of halogens or halogen compounds other than iodine or iodine compounds."

ERNEST SCHULTZ and E. L. SCHULTZ (New Zealand P. 61,918, Feb. 21, 1929) report to recover motor fuel from crude oil by a process consisting of

> "the use of an expansion-valve (preferably of the needle type) between a converter and a condenser so as to function to retard the gases from the converter and control the pressure of the gases in the converter before it is delivered to the condenser. A converter between the still or retort and the condenser, consisting of a combination of the metals nickel, lead, and zinc, or alternately nickel and zinc, with a metal capable of mixing into a homogeneous mass, or, alternatively, steel, the gases being kept under pressure by an expansion or needle valve. The feeding of lime, zinc chloride, or zinc oxide, with or without common salt or magnesium chloride or any other mixture suitable for reacting on the oils being treated, into the converter, and agitating the same in contact with the gases or vapours from the still or retort, the mixture being maintained under pressure."

5. CRACKING WITH HYDROGENATION.

It is reported that the extensive work of the I.G. Farbenindustrie A.-G. on the hydrogenation of carbonaceous material is to be applied by the Standard Oil Company of New Jersey to the hydrogenation of heavy oils. It is further stated that a plant[97] costing $5,000,000 with a capacity of 5000 bbls. of gasoline per day is to be constructed, and that a high yield of gasoline from heavy oils is obtainable.

Krauch[98] discusses the hydrogenation of hydrocarbons as carried out by the I.G. Farbenindustrie A.-G., but with only brief mention of oils.

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[97] *The Lamp*, June, 1929. Kirkpatrick, *Chem. Met. Eng.*, 1929, **36**, 332. *Oil Gas J.*, June 27, 1929, 44. Truesdell, *Nat. Petr. News*, July 10, 1929, 27.
[98] *Nat. Petr. News*, July 24, 1929, 69; July 31, 1929, 70; Aug. 7, 1929, 75.

Florian[99] questions the economy at the present of using so hazardous and expensive a process as hydrogenation of oils which is reported to require high temperatures and pressures of 100 to 300 atmospheres.

Smolenski and Badzynski[100] obtained 20 per cent. benzine and 20 per cent. naphtha by berginisation of asphaltic still residues from Polish paraffin oils. About 20 per cent. of other liquid fuel and 30 per cent. coke were the other products.

Ipatiew, Orlow, and Bielopolsky[101] cracked Grosny paraffinic residues under high hydrogen pressure at about 440° C. with initial pressures of 70 to 105 atmospheres rising to maxima of 220 to 265 atmospheres. Saturated products were obtained, including 34 per cent. of gasoline with end boiling point 150° C. (302° F.).

UNITED STATES PATENTS.

A. Debo (U.S.P. 1,704,792, Mar. 12, 1929) claims

"A process for maintaining continuously a definite liquid level in the interior of a high pressure chamber when splitting coal, oils and other hydrocarbons by heating these initial materials with hydrogen at a high pressure, consisting in converting said materials into a paste-like mass to a pressure of a few atmospheres, and then forcing it into the high pressure chamber, and subsequently drawing off the gaseous, liquid and solid products of reaction together from said high pressure container at a point located between the highest and lowest parts thereof."

W. L. Gomory (U.S.P. 1,670,804, May 22, 1928) has devised

"A process of cracking hydrocarbons consisting in forcing a mixture thereof with hydrogen through a conduit heated to a cracking temperature, maintaining a pressure in said conduit such that about 15 to 20 per cent. of the hydrocarbons remain in the liquid phase at the temperature employed, drawing off the resulting liquid, vapours and gases, separating the liquid and condensing the vapours."

I. W. Henry (U.S.P. 1,709,814, Apr. 16, 1929) arranges

"In apparatus for ionising and hydrogenating hydrocarbon vapour and oil, the combination with a chambered receiver provided with a surrounding coil for conducting a high frequency, oscillating, electric current effective to establish by induction a high frequency, oscillating, non-sparking, non-discharging, electro-magnetic field within the coil and chamber, a superheated steam generator provided with a discharge pipe discharging into said chamber, said chamber being provided with stationary, electric current conducting, sludge collecting and vapour heating elements, in electric current conducting proximity to one another, means for regulating the quantity of superheated steam delivered into said chamber, said elements also serving as short circuited secondaries in the electric circuit whereof said coil is a primary, the superheated steam generator being effective to dissociate into hydrogen and oxygen the superheated steam."

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[99] *Petr. Times*, 1929, **21**, 391.
[100] *Przemysl Chem.*, 1928, **12**, 117. *Chem. Abstr.*, 1928, **22**, 2834.
[101] *Brennstoff-Chem.*, 1929, **10**, 346.

I. W. HENRY (U.S.P. 1,709,815, Apr. 16, 1929) cracks hydrocarbon fluids and solids by

"Simultaneously dissociating electrically resistant starting material into free hydrogen and free carbon; dissociating superheated steam into hydrogen and oxygen; and subjecting the dissociated constituents to the co-action of a high frequency, oscillating, non-sparking electro-magnetic field, in a place of partial confinement, wherein the pressure is solely due to expansion of the vapours, gases or liquids produced; and in varying the cycles of said electro-magnetic field and thereby stratifying the gaseous vapours in the place of partial confinement."

MAX HOFSASS (U.S.P. 1,729,943, Oct. 1, 1929) claims a

"Process for simultaneously hydrogenating and purifying mineral oils which comprises submitting the same to the combined action of hydrogen and metallic sodium under super-atmospheric pressure and at a temperature of at least about 300° C."

E. A. PRUDHOMME (U.S.P. 1,711,855, May 7, 1929) claims

"A process for manufacturing liquid fuels which consists in subjecting hydrocarbon vapours to a staged catalysis in a series of catalysers which effect in successive catalysers a general hydrogenation of said products, a dehydrogenation or a splitting up of said products into unsaturated hydrocarbons, and a saturation and polymerisation of said products."

E. A. PRUDHOMME (U.S.P. 1,711,856, May 7, 1929) devises

"A process for the manufacture of synthetic fuels which consists in vaporising hydrocarbon products and passing said vaporised products through a series of successive catalysers to a condenser, said catalysers effecting in successive steps a general hydrogenation, a splitting up of the hydrogenated products into unsaturated products, and a saturation and polymerisation of said unsaturated products, the step of adding to said vaporised products before entry into each catalyser variably proportioned amounts to reducing gas."

W. E. SHORE (U.S.P. 1,687,595, Oct. 16, 1928) presents

"A process for converting heavy hydrocarbons to light hydrocarbons, comprising directing the oil through the jacket of a compressor, then introducing same in the presence of hydrogen bearing gases to a mechanically operating atomiser, then conducting the produced vapour to the compressor cylinder and raising its temperature under compression, then passing the highly heated vapour to expansion condensers."

The compressor is stated to raise the temperature of the vaporised mixture from 800° to 1200° F.

M. J. TRUMBLE (U.S.P. 1,725,320, Aug. 20, 1929) includes in a cracking apparatus

"An equilibrium chamber provided with an outlet for lighter fractions, a hydrogenator disposed above and delivering directly thereto, and means independent of means for supplying new materials for repeatedly passing heavier fractions back from said chamber through both said hydrogenator and said chamber."

AUSTRALIAN PATENTS.

R. T. Haslam and R. P. Russell (Australian P. 17,774, Sept. 10, 1929) reveal that

"To produce valuable products from oils, such as crude petroleum and the like, the oil is forced from a line into a coil in which it is heated to a temperature of about 750°—950° F., and is discharged therefrom at a pressure of about 50 or 100 atmospheres or more (preferably about 200 atmospheres) into the bottom of a reactor where it is intimately commingled with hydrogen, injected through a line, the hydrogen having been heated in a heat exchanger. Catalytic substances such as finely divided heavy metal oxides are provided in the reactor and/or coil and are maintained in suspension by recirculation of oil through the lines. Vapours pass from the reactor through the heat exchanger and condensers, the condensate drawn off through the line passing to the recirculating line and that from the condensers to cooler, from which kerosine and gasoline respectively are withdrawn. Hydrogen and any other remaining gases pass through purifying towers and thence back into the system."

I. G. Farbenindustrie A.-G. (Australian P. 16,917, Aug. 6, 1929) discloses

"A process for the manufacture and production of valuable hydrocarbons from coal pastes, mineral oils, tars, and the like, and the distillation, conversion products, and residues thereof, which initial materials may be sulphur bearing or may contain products of asphaltic nature, consists in first treating the said initial materials in liquid form with hydrogen or gases supplying the same, under such conditions of temperature and pressure, preferably in the presence of catalysts, that the sulphur and oxygen present as such or in the form of their compounds are completely or for the most part eliminated, and then subjecting the resulting products to a cracking treatment and with or without catalysts."

I. G. Farbenindustrie A.-G. (Australian P. 17,320, Aug. 6, 1929) reports

"To produce valuable hydrocarbons, by the treatment of carbonaceous materials in the liquid state, such as suspensions or pastes of coal, tars, mineral oils, and the like, with hydrogenating gas in the presence of a catalyst immune to sulphur poisoning, an intensive state of motion is imparted to the materials under treatment so that no injurious local thickening occurs."

I. G. Farbenindustrie A.-G. (Australian P. 17,450, Aug. 13, 1929) claims

"A process for the manufacture and production of valuable liquid products from varieties of coal, tars, mineral oils, their distillation, extraction, and transformation products, residues, and the like by a treatment with gases containing hydrogen, substantially in the absence of carbon monoxide and of such substances as lead to the formation of carbon monoxide in the reaction at an elevated temperature and under a pressure of at least 50 atmospheres, while excluding injurious iron, nickel, and copper, the last named only when sulphur is present, from the reaction chamber, and if desired, such other parts of the apparatus as come into contact with the reaction mixture at temperatures above 300° C. The reaction chamber or other parts of the apparatus in question are coated with or constructed of aluminium or high aluminium alloys, or with chromium, molybdenum, tungsten, vanadium, or alloys containing chromium, molybdenum, tungsten, vanadium, or manganese, or

several of these elements, with, if desired, a considerable proportion of nickel and a low carbon content, or with carbides of refractory metals, especially those of groups 5 and 6 of the periodic system."

H. TERRISSE and L. DUFOUR (Australian P. 18,355, Oct. 1, 1929) devise

"A process for the conversion of high boiling hydrocarbons into low boiling hydrocarbons consisting in heating the former to 200—500° C. in the presence of ferrous chloride and of such gases as hydrogen, water gas, and like gases under a pressure of from 5 to 40 kilograms per square centimeter, the desulphurisation of the hydrocarbons occurring simultaneously. The reaction can be accelerated by the addition of active coal, brown coal, or peat. Sufficient ferrous chloride must be added to combine with the sulphurets present and leave a surplus for the catalysis."

BRAZILIAN PATENTS.

STANDARD OIL DEVELOPMENT CO. (Braz. Appl. 6,219, Jan. 20, 1929) claims

"That oil to be hydrogenated is preheated and introduced under pressure to the reaction vessel, where it is intimately mixed with a catalyst and hydrogenated at 750–850° C. and 100–200 atmospheres pressure. Gases and vapours withdrawn from the reaction zone are heated and returned to the process together with fresh oil. The light boiling products are condensed and recovered and hydrogen containing gases returned to the process."

STANDARD OIL DEVELOPMENT CO. (Braz. Appl. 6,994, July 5, 1929) obtains

"Low boiling hydrocarbons from oil or carbonaceous material by a combination of cracking and hydrogenation in a cycle process. The raw material is hydrogenated at about 50 atm. and 450–950° F., the product fractionated and the high boiling fractions cracked. This cracked product is again fractionated and the residue hydrogenated."

CANADIAN PATENTS.

I. G. FARBENINDUSTRIE A.-G. (Can. P. 288,073, March 19, 1929) claims a

"Process for the production of valuable hydrocarbons from liquid carbonaceous material, which initial material may be sulphur containing or may contain asphaltic constituents which consists in first treating the said initial materials in liquid form with hydrogen under an elevated pressure and at temperatures of between about 400° and 480° C. in the presence of a catalyst containing molybdenum and chromium in such a manner and only for so long a time that the compounds of sulphur and oxygen therein are substantially eliminated, and that no substantial disruption of the carbon skeleton of the molecule and no substantial destructive hydrogenation of the material occurs, and then subjecting the resulting products to a cracking treatment."

I. G. FARBENINDUSTRIE A.-G. (Can. P. 292,797, Sept. 10, 1929) claims

"In the conversion of hydrocarbons of high boiling point range into others of low boiling point range, the step which consists in acting on the said materials with an addition of catalysts of the type of the complex ansolvo acids, the process being carried out in the presence of hydrogen."

V. W. NORTHRUP (Can. P. 287,912, Mar. 12, 1929) reports a

"Method of converting heavier hydrocarbons into lighter hydrocarbons which comprises producing a mixture of vapours of said heavier hydrocarbons and a gas having available hydrogen, subjecting the same to an alternating current field of 2,000 to 8,000 volts in one zone, whereby the reaction mass is electrified without substantial cracking taking place, and then catalysing at temperatures of about 725° F. to 1,000° F. in another zone which is independent of said first mentioned zone."

ENGLISH PATENTS.

J. M. F. D. FLORENTIN and A. J. KLING (E.P. 308,712, May 23, 1929, not yet accepted)

Present a process for obtaining motor spirit by hydrogenating heavy organic compounds under pressure in which "the whole or a part of the heat necessary to bring the reaction chamber to the required temperature is furnished by admitting compressed hydrogen to the chamber at a temperature above the normal reaction temperature."

FOHLEN (E.P. 313,963, Aug. 4, 1929, not yet accepted) finds that

"Light hydrocarbons are obtained from natural or industrial fuels and carbonaceous materials by simultaneous cracking and treatment with nascent hydrogen under pressures from 5 atmospheres to superpressures and at temperatures from 200° C. to 1,000° C. The nascent hydrogen is produced by the decomposition of hydrogen-containing bodies. In an example, water is used as the source of hydrogen; shale oil distilling from 260° C. upwards is stirred with an aqueous solution of metal halides, iron filings and copper or brass shavings for 4 hrs. at 300–400° C. and 120–180 atmospheres pressure. The product yields 50 per cent. of light oil of density 0·850 distilling below 200° C. and 42 per cent. of oil of density 0·870 distilling between 200° C. and 300° C. Similar results are obtained by the use of temperatures of 500–600° and pressures of 20–30 atmospheres."

K. GORDON and IMPERIAL CHEMICAL INDUSTRIES (E.P. 309,239, May 29, 1929) perform

"The destructive hydrogenation of carbonaceous materials under pressures greater than 1,000 atmospheres. Preliminary hydrogenation may be performed at 200–1,000 atmospheres, the products thus obtained being heated at 4,000–5,000 atmospheres or even at 10,000 atmospheres."

K. GORDON and IMPERIAL CHEMICAL INDUSTRIES (E.P. 315,513, Sept. 4, 1929) present the improvement that

"In the destructive hydrogenation of oil or coal and oil mixtures the wall of the reaction chamber is cooled by flowing over it a stream of the relatively cool material to be hydrogenated."

HOFMAN and WULFF (E.P. 301,395, Jan. 23, 1929, not yet accepted) use

"The halogenides of boron or their addition or substitution products as catalysts in cracking processes in the presence or not of hydrogenating gases. 1,000 parts by weight of a crude mineral oil are cracked in the presence of 5 per cent. of boron fluoride at 350° C. and 150 atmospheres. 75 per cent. of the product boils below 250 while 15 per cent. consists of a highly viscous lubricating oil."

G. HUGEL, M. PAUL and M. BOISHEL (E.P. 286,206, Apr. 25, 1928, not yet accepted) report that

"The hydrogenation of organic substances, particularly the products of distillation of coal and petroleum is effected by means of hydrides of alkali, or alkaline earth metals whether ready made or produced in it during the process. The process may be effected below 300° C. and 100 kilos pressure and is not affected by the presence of contact poisons such as nitrogen, sulphur, arsenic and oxygen compounds."

A number of the English patents to the I.G. Farbenindustrie, A.-G., covering destructive hydrogenation of carbonaceous materials, include liquid stocks such as mineral oils, among the usable charging stocks, and operate at such temperatures that it is probable that cracking occurs. Summaries of these patents are as follows:

E.P. 286,679 (May 2, 1928) sets forth that

"In the production of benzine-like hydrocarbons by the destructive hydrogenation of coal, tars, mineral oils, and similar carbonaceous substances, at pressures of at least 50 atmospheres, the catalyst used contains a compound of cadmium, lead, bismuth, or tin, with or without difficulty reducible metal oxides or carbonates forming such oxides, and with or without metals or compounds of metals of the 8th group of the periodic system. Iron and carbonates of magnesium, lithium, manganese, vanadium, zinc, and uranium are specified. In an example, fuel oil is passed continuously with hydrogen and nitrogen at 200 atmospheres and 500° C. over porous material impregnated with lead nitrate."

E.P. 286,680 (May 2, 1928) provides that

"In the production of benzine-like hydrocarbons by the destructive hydrogenation of coal, tars, mineral oils, and similar carbonaceous substances at pressures over 50 atmospheres, the catalyst used contains an oxide or carbonate of uranium, with or without metals, or compounds of the metals, of the 8th group of the periodic system."

E.P. 288,148 (May 23, 1928, not yet accepted) covers the heating of

"The residues remaining after the destructive hydrogenation of coals, and tars to recover the oily constituents. The temperatures used may be sufficiently high to crack the oils and produce benzines or to produce permanent gases, *e.g.*, olefines."

E.P. 287,855 (May 23, 1928, not yet accepted) arranges that

"In the destructive hydrogenation of coal, oils, etc., the temperature of the reaction is regulated partly directly by the temperature of the hydrogenating gas introduced into the reaction chamber and partly indirectly by the temperature of materials not introduced into the reaction chamber but brought into contact with the reacting materials in other parts of the apparatus."

E.P. 295,587 (Oct. 10, 1928) reports

"The destructive hydrogenation of coals, tars, and products thereof at a pressure of at least 20 atmospheres, and preferably at 50 atmospheres, in the presence of a catalyst consisting of lead or tin or their compounds on supports of magnesia or magnesite. The catalysts may be used alone or mixed with other substances. Gases containing combined hydrogen capable of being set free in the reaction vessel may be used in place

of hydrogen, but care must be taken that those parts of the apparatus which come in contact with the hot reacting materials are free from substances which would lead to the formation of methane and the separation of carbon. The process may be carried out in the liquid or vapour state, and the material to be treated may rest on porous plates."

E.P. 295,974 (Oct. 17, 1928) cracks

"Oils by heating them in a still by a heating device immersed in the liquid and exposed to intermittent or continuous blasts of gases supplied through a pipe. The heater is composed of a rod, spiral, or ribbon of metal or other conductive material, e.g., silicon carbide, graphite, charcoal, etc., and is heated to at least 500° C. by electrical or other means. The gases may contain oxygen, hydrogen, or gases and vapour capable of giving off hydrogen but free from carbon. Brown coal tar pumped from a container and preheated in a vessel is passed through a pipe into the still which is heated externally to 350° C. The heater, consisting of a nickel-chromium ribbon, is raised to 750° C. by an electric current supplied through copper conductors and is treated with a blast of steam from the pipe. The vapours produced are condensed in a cooler while the gaseous products pass to a holder. In another example crude paraffin is treated in a similar manner."

E.P. 296,431 (Oct. 24, 1928, not yet accepted) states that

"Hydrocarbons of low boiling point are obtained by treating coal suspensions, tars, oils, etc., with hydrogen in several stages of diminishing pressure, the reaction product from a former stage being subjected to lower pressure in the following stage and the initial materials are exposed at least in the first stage to hydrogenation in the liquid phase under high pressure while the products in the final stage are heated in the vapour phase at low pressures. American crude mineral oil containing 40–50 per cent. of constituents boiling above 350° C. is treated in the liquid phase with hydrogen at 200 atmospheres and at 450° C. in the presence of a catalyst containing molybdenum and chromium. The product is expanded into a second reaction chamber maintained at 20 atmospheres and 480° C. About 75 per cent. of the products obtained are benzenes boiling below 200° C. In treating heavy oils containing asphaltum pressures of over 1000 atmospheres are used and several stages are employed."

E.P. 300,703 (Jan. 9, 1929) carries out

"The destructive hydrogenation of carbonaceous materials in the presence of a catalyst containing 10 per cent. of a mixture of copper and zinc or copper and cadmium the remainder being made up of one or more of the elements boron, aluminium, silicon, titanium, vanadium, tantalum, chromium, molybdenum, and tungsten or their compounds or compounds of cobalt. Large excess of hydrogen or hydrogenating gases are used preferably in a circulatory system. Crude oil mixed with Florida earth is treated with hydrogen whilst stirring under a pressure of 200 atmospheres and at 420° C. and the vapours produced are led over a catalyst consisting of silicic acid with 10 per cent. of a mixture containing about 30 per cent. copper and 70 per cent. zinc. A product is obtained containing 70–80 per cent. benzene."

E.P. 301,059 (Jan. 16, 1929, not yet accepted) provides that

"In the destructive hydrogenation of carbonaceous materials the products to be treated are passed through a series of reaction vessels, i.e., more than two, arranged one behind the other so that no appreciable cooling of the reacting materials occurs between separate vessels."

E.P. 302,253 (Feb. 6, 1929) obtains

"Hydrocarbon mixtures boiling below 200° C. and consisting mainly of aromatic and unsaturated aliphatic and hydro-aromatic compounds by acting on carbonaceous materials containing substantial amounts of non-aromatic hydrocarbons, e.g., coals, tars, mineral oils, pitches and their conversion products, at temperatures above 550° C., and at pressures above 20 atmospheres in the presence of excess hydrogen and preferable in the presence of catalysts. If the latter are used they should be of the kind exerting a 'cracking' reaction, e.g., elements of the third and fourth groups of the periodic system and elements of the second group in conjunction with ruthenium chloride."

E.P 304,343 (Mar. 13, 1929) devises that

"In the production of hydrocarbons of low-boiling point by heating carbonaceous materials in the presence of gases and/or vapours, in particular in the destructive hydrogenation of coals, tars, oils, etc., or in the low temperature carbonisation of coal in the presence of gases, the gases and vapours are maintained at a higher rate of flow in the reaction space than they would have by being merely passed through the reaction chamber. The increased flow is obtained either by setting up a pulsating or oscillating movement of the gases in the reaction space, or by repeatedly circulating the gases in the reaction chamber through the reaction space."

E. P. 305,553 (April 4, 1929) obtains lubricating and insulating oil

"From coal, tars, mineral oils, and other carbonaceous materials by extracting or destructively hydrogenating the solid materials or cracking or destructively hydrogenating the liquids, and exposing the liquid products or fractions thereof, in the coherent liquid phase, to the action of high-tension and preferably high-frequency electric currents."

E. P. 307,956 (May 8, 1929) obtains hydrocarbons of low boiling point

"From carbonaceous materials, e.g., coals, tars, mineral oils, etc., by heating such materials to about 450°C. in the presence of catalysts comprising oxides of the metals or metalloids of groups 3-7 deposited in small amounts on the metals, aluminium, silver, manganese, chromium, or chromium-nickel alloy. The reaction is preferably conducted under high pressure, e.g., 200 atmospheres, and in the presence of hydrogen or gases containing hydrogen."

In an example

"Mineral oil boiling above 270°C. is passed with excess hydrogen as 450°C. and 200 atmospheres through an aluminium lined vessel containing a catalyst comprising aluminium granules activated with 1-2 per cent. of uranyl nitrate."

E. P. 309,228 (May 29, 1929) carries out

"The destructive hydrogenation of carbonaceous materials in the presence of small quantities of organic surface-tension reducing agents containing the radical of a mineral acid in the molecule such as aromatic and aliphatic sulphonic acids, and sulphonic acids of aromatic or hydro-aromatic hydrocarbons sulphonated in the nucleus and containing at least one alkyl group in the nucleus. Specific examples are sodium isopropyl naphthalene sulphonate, phenyl borate, the residues obtained by evaporating sulphite cellulose waste liquor, and the sulphonated

products of destructive hydrogenation. Other substances having a catalytic action such as alkalis, magnesia, or zinc oxide may be added. The operation may take place under pressures of 50-200 atmospheres."

E. P. 311,251 (July 3, 1929) states that

"Catalysts, comprising metals and their compounds, particularly those belonging to the sixth group, are activated before use in destructive hydrogenation or cracking by heating them for several hours at 300-600° C. in the presence of gases which have no reducing action upon them, e.g., carbon dioxide, sulphur dioxide, nitrogen oxides, oxygen, air, nitrogen, etc. A middle oil is passed with hydrogen at 450°C. and 200 atmospheres pressure over a catalyst prepared by heating tungstic acid with nitric oxide at 350°C. Other suitable catalysts are molybdic acid activated by heating with carbon dioxide or sulphur dioxide, molybdic acid and silicic oxide heated in nitrogen, cobalt oxide and chromium oxide activated by carbon dioxide, and molybdenum wire wool activated by treatment with oxides of nitrogen."

E. P. 311,628 (July 10, 1929, addition to E. P. 282,384) covers

"The improvement in the parent Specification consisting in lining such parts of the apparatus as come into contact with sulphur contaminated hydrocarbons with silver and its alloys."

E. P. 311,789 (July 10, 1929) employs

"Complex 'ansolvo' acids or their components as catalysts in the destructive hydrogenation or cracking of carbonaceous materials. An 'ansolvo' acid is an acid substance obtained by mixing an organic acid with an inorganic salt so that a complex body is formed which has the power of setting free hydrogen ions and is characterised by liberating nitrogen from diazo-acetic acid. Temperatures of 350-600° and pressures varying from atmospheric to 1,000 atmospheres may be used. 100 parts of a tar fraction boiling between 300-500°C. are treated with 5 parts of a double compound of alpha naphthoic acid and tin tetrachloride at 350-400°C., and 10 atmospheres pressure and a product was obtained 41 per cent. of which boiled under 200°C."

Imperial Chemical Industries (E. P. 309,095, May 29, 1929) states that

"The destructive hydrogenation of carbonaceous materials is carried out at pressures of from 300-1,000 atmospheres. When pressures of 300-500 atmospheres are used a temperature of 420°C. is preferably employed while higher temperatures of 450-500°C. are used in conjunction with pressures of 50 to 100 atmospheres." (cf. E. P. 309,258—apparatus similar.)

Kohlenveredlung Akt-Ges. (E. P. 293,430, August 29, 1928, not yet accepted) states that

"Oils, tars, etc. are distilled or cracked by feeding them through a pipe onto discs rotating in a vessel between fixed plates so that they are atomised by the rotation of the discs, hot gases or vapours being simultaneously circulated through the vessel. The mixed vapours and gases pass out of the treatment vessel through a pipe and are recirculated through a heater by a pump, part of the products being periodically withdrawn through a pipe to a condenser. If hydrogenation of the materials is required, gases containing hydrogen, e.g., water gas, are used as the heating gases and the process is carried out under pressure and in the presence of catalysts."

E. C. R. Marks (E. P. 299,347, Dec. 19, 1928) cracks and hydrogenates oils

"By passing them after heating in counter current to a flow of heated gas, e.g., steam, the mixed gases being re-heated in a separate chamber and finally passed upwards through a stream of crude oil."

A. Rule, H. G. Watts and Imperial Chemical Industries (E. P. 317,346, October 9, 1929) state that

"Light hydrocarbon oils are obtained from tar sands by extracting their carbonaceous content with solvent and submitting the extract, with or without removal of the solvent, to destructive hydrogenation in a known manner."

Standard Oil Development Company (E. P. 304,301, March 13, 1929, not yet accepted) converts

"Carbonaceous materials, e.g., oils, coal suspensions, etc., into hydrocarbons of low boiling point by bringing them into intimate contact with hydrogen at high temperatures and pressures in a reaction zone, a portion of the converted material being withdrawn from the reaction zone, re-heated and returned thereto. The reaction is preferably conducted in the presence of catalysts, e.g., metallic oxides, which are circulated with the oil or introduced into the reaction chamber."

Standard Oil Development Company (E. P. 304,796, March 20, 1929, not yet accepted) obtains

"Light hydrocarbons from oils by heating the oil under a pressure of at least 50 atmospheres in presence of hydrogen, withdrawing the vapours and liquids produced, and continuously distilling the liquids in a plurality of distillation zones."

Standard Oil Development Company (E. P. 304,797, March 20, 1929, not yet accepted) obtains

"Light hydrocarbons from oils by distilling a fraction from the oils under low pressure, hydrogenating the residual oil under elevated pressure, and returning the hydrogenated product to the distillation zone."

Standard Oil Development Company and F. A. Howard (E. P. 308,297, May 15, 1929) state that

"White oils and other highly purified petroleum oils are obtained by subjecting a crude petroleum or a heavy fraction thereof to hydrogenation, and maybe cracking, by treatment with hydrogen at a high temperature and pressure, separating the product having a viscosity of about 50-600 secs. Saybolt at colour, taste, and odour. In an example, Pennsylvania crude oil is treated at 750-850°F. and 50-100 atmospheres. Preferably the oil is agitated by continuous injection of hydrogen. The process may be continuous or by batches in a reactor having non-reactive steel alloy surfaces. Metal oxides or other catalysts, e.g., a mixture of 9 lb. of chromium oxide with 1 lb. of molybdenum oxide, should be suspended in the oil.

H. Terrisse and L. Defour (E.P. 305,981, Apr. 10, 1929, not yet accepted) claim that

"Oils of high boiling point, e.g., gas oil, lamp oil, schist oil, brown coal tar, etc., are converted into motor benzine by heating them at 200-500°C. under pressure of 5-40 kilogrammes per sq. cm. in the presence of ferrous chloride and gases such as hydrogen, water gas, etc., the desulphurisation of the oils proceeding simultaneously."

FRENCH PATENTS.

I. G. FARBENINDUSTRIE A.-G. (Fr. P. 659,583, August 28, 1928)

"Claims to obtain valuable hydrocarbons from mineral oils, tars, etc., or their distillation products, by treating the initial materials preferably in the liquid state with hydrogen or gases capable of liberating it, and preferably in the presence of catalysts and at such temperatures and pressures that sulphurised and oxygenated compounds are eliminated, then submitting the products to cracking in the absence of hydrogen and with or without catalysts."

I. G. FARBENINDUSTRIE A.-G. (Fr. P. 659,584, August 28, 1928)

"States that valuable hydrocarbons are obtained by treating carboniferous suspensions, tars, mineral oils, etc., or their transformation products with hydrogen at high temperature and pressure, preferably in the presence of catalysts, in several steps, each step taking place under a pressure less than that of the preceding one."

I. G. FARBENINDUSTRIE A.-G. (Fr. P. 659,906, Sept. 3, 1928)

"Reports that hydrocarbons such as mineral oils, tars, etc., are converted into products of low boiling point by cracking with or without addition of hydrogen, and under such conditions that a carbonaceous precipitate is formed, without formation of much gas, and treating the products still charged with the formed deposit, preferably in the liquid state, with hydrogen or gases yielding it immediately afterward at a high temperature and under high pressure with or without catalysts."

GERMAN PATENTS.

A. DEBO (D. R. P. 469,857, December 29, 1928) states that

"Hydrocarbons are cracked or hydrogenated by heating under high hydrogen pressure in an apparatus from which the gaseous, liquid and solid reaction products are removed together from one end of a cylindrical reaction chamber through a common immersed outlet tube which maintains a constant liquid level necessary for the proper reaction. The hydrogen and liquid or pasty raw material enters at the top or bottom of the other end of the retort. A thorough mixture and slow movement of the material through the chamber is obtained by a mixer rotating on a horizontal shaft and provided with vertical discs which leave only a narrow space at the circumference of the chamber through which the material can move towards the outlet."

ERDOL UND KOHLE-VERWERTUNG A.G. (D. R. P. 469,228, Dec. 13, 1928)

"Discloses a process of desulphurising and hydrogenating heavy mineral oils or distillates by heating it above 300° with an alkali metal and hydrogen under pressure, and if necessary with the addition of a porous material as charcoal, powdered coke, or Fuller's earth whereby a splitting of the molecules takes place."

6. CRACKING WITH OXIDATION.

Claims of a number of patents cover cracking in combination with oxidation, either oxidising with cracking or causing the primary products of decomposition to react with oxygen or air.

UNITED STATES PATENTS.

O. C. Brewster (U.S.P. 1,681,658, Aug. 21, 1928) includes

"In apparatus for conversion of hydrocarbon oils, means for maintaining a body of oil under pressure and at conversion temperature, means for conducting vapours away from said chamber, means for maintaining a separate pool of oil, means for passing heated oil from said body of oil to said separate pool of oil whereby the oil in said separate pool is brought to oxidising temperature, means for supplying an oxidising gas to said separate pool of oil, means for continuously supplying fresh oil to said separate pool, and means for removing oil from said separate pool of oil and conducting it into said body of oil."

"Suitable pressures may be, for example, from 100 to 300 pounds gauge. The temperatures employed are in excess of about 650° F., and preferably about 720 to 760° F. Higher temperatures may be employed, if desired; for example, temperatures ranging to 850° F. or higher."

O. C. Brewster (U.S.P. 1,694,092, Dec. 4, 1928) claims

"The method of converting hydrocarbon oils which comprises maintaining a body of oil under pressure and at conversion temperature by internal oxidation within the body of oil, removing vapours therefrom, heating a flowing stream of oil to conversion temperatures by supplying an oxygen containing gas in contact with said stream of oil, and passing said heated stream of oil before substantial conversion thereof into the body of oil."

The same pressures and temperatures as in U.S.P. 1,681,658 are given.

Gustav Egloff and J. C. Morrell (U.S.P. 1,733,656, Oct. 29, 1929) claim

"A process for treating hydrocarbon oil to produce a lower boiling point distillate and a substantial quantity of oxidation products, consisting in subjecting the oil, while under a superatmospheric pressure, to a temperature sufficiently high to cause substantial vaporisation of the oil under such pressure, in effecting the heating of the oil and the vaporisation thereof in the presence of a metallic oxide, in condensing the heavier fractions of the evolved vapours, in injecting into the condensed heavier fractions an oxidizing gas, and in then returning the condensed heavier fractions to the oil undergoing heat treatment in the process."

Carleton Ellis (U.S.P. 1,697,265, Jan. 1, 1929) presents

"The process of oxidation which consists in subjecting in the vapour state derivatives of petroleum hydrocarbons obtained by cracking to the action of oxygen in the presence of a catalyst at a temperature of incipient redness, whereby intermediate products of oxidation other than ordinary products of combustion are obtained."

"The range of temperature employed in accordance with the present invention may be set broadly (that is, with wide limits) at from 840° F. (450° C.) to about 1000° F. (538° C.). Preferably, however, the temperature is kept within narrower limits; *e.g.*, 910° F. (488° C.) to 970° F. (521° C.)."

Maleic, phthallic, citraconic, benzoic, propionic, and formic acids, formaldehyde, acetaldehyde and benzaldehyde, are mentioned as among the products obtained.

CARLETON ELLIS (U.S.P. 1,697,266, Jan. 1, 1929) describes a process which includes

"Oxidation of kerosine oil by treatment with an oxygen-containing gas at a temperature below a red heat under conditions to produce substantial oxidation and collection of the oxidised products, the step of using an amount of oxygen sufficient to oxidise only a minor portion of the hydrocarbons of said kerosine oil."

Cracking to gasoline and gases may be a part of the process.

CARLETON ELLIS (U.S.P. 1,697,267, Jan. 1, 1929) presents

"The process of making oxygenated aliphatic bodies which comprises passing gas from cracking petroleum into contact with a heated catalyser maintained at just below dull redness, and in the presence of an oxygen-containing gas, the mixture containing substantially more than one atom of oxygen to each molecule of readily oxidisable constituents in said gas, to effect selective oxidation."

HARALD NIELSEN (U.S.P. 1,672,081, June 5, 1928) devises

"The process of converting hydrocarbons while in gaseous form into other compounds which consists in passing the same over a copper suboxide while maintaining a temperature of from 250° C. to 800° C."

C. S. PALMER (U.S.P. 1,699,627, Jan. 22, 1929) claims as new

"The continuous process of making by-products from inactive and inert oil or gas, which consists in cracking such oil or gas and thereby vaporising and rendering the hydrocarbon constituents more active and capable of oxidation, preheating oxidising gas by heat from the cracking, and then partially oxidising the hydrocarbon constituents with such preheated gas."

CANADIAN PATENTS.

O. C. BREWSTER (Can. P. 288,889, Apr. 16, 1929) reported an apparatus for the conversion of hydrocarbon oils consisting of

"Means for maintaining a body of hydrocarbon oil under pressure and at conversion temperature, means for maintaining a plurality of separate pools of oil apart from said body of oil, means for flowing oil successively through said separate pools of oil, means for causing an oxidising gas to pass in contact with said separate pools of oil in countercurrent to the direction of flow of oil therethrough."

O. C. BREWSTER (Can. P. 292,831, Sept. 3, 1929) devises a

"Method of converting hydrocarbon oils which comprises maintaining a body of oil, circulating oil from said body in a confined stream through a heating zone and back to said oil body until the oil body is brought to a temperature of active oxidation in the presence of an oxygen-containing gas, discontinuing said circulation of the oil, supplying into the body of oil controlled quantities of oxygen-containing gas while maintaining upon the body of oil a pressure of at least 4 atmospheres, removing vapours evolved from the body of oil, and supplying to it additional oil preheated to approximately the temperature of the body of oil."

R. J. DEARBORN (Can. P. 290,032, May 28, 1929) describes a

"Process of decomposing organic material in a substantially liquid state, which comprises maintaining the liquid in a heat insulated converting vessel at a temperature and pressure suitable to active decomposition thereof, introducing an oxidising gas to react exothermically with the liquid therein, removing the generated vapours and condensing therefrom the less volatile constituents, collecting the condensate and raising it to a high temperature and pressure to effect liquid phase cracking thereof, reducing the pressure and temperature of the cracked condensate to substantially that temperature and pressure obtaining in the converting vessel and passing the cracked liquid into the converting vessel to undergo further decomposition therein."

G. W. GRAY and R. J. DEARBORN (Can. P. 286,552, Jan. 15, 1929) describe a

"Process of decomposing organic materials in a substantially liquid state, which comprises introducing the liquid into a heat-insulated converting vessel maintained under conditions of pressure and temperature suitable to active decomposition, removing the generated vapours in heat exchange relationship with the fresh charge and condensing therefrom the less volatile constituents, raising the condensate to a cracking temperature without substantial decomposition, introducing the heated condensate into the vessel for further treatment, and compensating for heat losses in the vessel to maintain a substantially constant predetermined decomposition temperature therein by introducing regulated quantities of an oxidising gas."

ENGLISH PATENTS.

A. FECHTER and P. BURGER (E.P. 295,938, Oct. 17, 1928, not yet accepted) present

"Apparatus for splitting oils or obtaining oil gas by igniting a mixture of hydrocarbons and hydrogen in a chamber."

P. GIRARD, F. PETIT and A. CHARBONNEAU (E.P. 299,861, Dec. 28, 1928) distil liquid combustibles to give light hydrocarbons including petroleum, in the presence of a substance which gives off nascent oxygen on heating. The reaction may be assisted by ionisation of the vapours by high frequency discharges, tension of 1,000,000 volts being mentioned. Addition to E.P. 290,606.

7. CRACKING OF NATURAL GAS.

The production of motor fuel or aromatic hydrocarbons for other uses by the cracking of natural gas has been studied by a number of investigators. Brooks[102] writes: "Gases comparatively rich in hydrocarbons other than methane give much better yields of benzol than those high in methane. Pure ethane yields about 25 per cent. of condensable products at 800—900° C. The cracking of butane is carried out industrially for production of ethylene and propylene, which is used for the manufacture of somewhat more than 30 tons per day of the corresponding glycols and related

[102] *J. Inst. Petr. Techn.*, 1928, **14**, 743.

compounds. Although few dependable analyses of natural gas have been made upon which an estimate might be made, the amount of ethane, propane, and butane certainly exceeds the amount of recoverable gasoline in natural gas, probably five fold. The operation of these two processes therefore offers the possibility of producing an excellent anti-knock motor fuel in quantities about equal to the amount of natural gas gasoline now produced."

Burrell[103], reviewing past work in this field, has pointed out that the conversion of paraffin, and olefine, and naphthenic hydrocarbons, as well, into aromatics under high temperatures has been long known and is a basically non-patentable operation.

Fischer[104] formed aromatic hydrocarbons, including benzene, toluene, xylene, naphthalene, anthracene, and phenanthrene, by heating methane for regulated periods at temperatures of 1000 to 1100° C. in porcelain or quartz tubes. He found the period of heating to be fully as important as the temperature. He thought of the process as taking place in two parts, first, a splitting of the methane molecule and second a recombination of the cleavage products. There is an optimum temperature for splitting the methane and a different optimum temperature for the synthesis of the cleavage products. Analogously there is also an optimum period of heating for a given cracking temperature and an optimum heating period for that temperature at which the radicals combine. The kind of product that results depends on the radicals into which the methane molecule is broken and under what conditions these radicals can combine. Catalysers appear to be of no assistance in avoidance of carbon separation, but during the cooling periods they influence polymerisation of the radicals. Pressure, similarly, is a disadvantage in cracking but an aid in the polymerising process. Fischer's yields of oil and tar attained 13 per cent. of the methane passed through the apparatus.

Stanley and Nash[105] confirmed Fischer's results and found methane to yield on subjection to passage through a silica tube at 1100° C. approximately 10 per cent. of liquid and solid hydrocarbons, calculated on the original methane. "For each temperature there is a heating period which gives optimum yields of higher products, the duration of which is decreased by rise in temperature." The best yields of higher hydrocarbons were obtained at a temperature of 1150° and a heating duration of 0·6 second." Under these conditions the yield of a light oil and

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[103] *Nat. Petr. News*, Jan. 9, 1929, 79.

[104] *Brennstoff-Chem.*, 1928, **9**, 309. *Chem. Markets*, 1928, **23**, 587. *Second Intern. Conference Bituminous Coal*, 1928, II, 789. See Fischer and Bahr, *Ges. Abhandl. Kenntnis Kohle*, 1924-7, **8**, 274 (published 1929).

[105] *Nature*, 1928, **122**, 725. *J.S.C.I.*, 1929, **48**, 1T.

tar was 11·0 per cent. calculated on the methane used, whilst the quantities of acetylene and ethylene in the reaction gas corresponded with a total conversion of methane into these gases of 8·8 per cent. and only about 6 per cent. of the methane was converted into its elements. The yield of light oil was 4·8 per cent. or 0·2 gallon per 1000 cubic feet of methane."

Wheeler[106] claims priority over Fischer in the production of benzene from methane. Wheeler and Wood[107] observed that liquid hydrocarbons were formed during the passage of methane through a quartz tube at temperatures higher than 875° C. Benzene was found to be an important product of the pyrolysis of methane between 875° and 1100° C., the optimum temperature appearing to be about 1050° C., and the best yield about 0·2 gallon per 1000 cubic feet of methane.

Chamberline and Bloom[108] formed aromatic hydrocarbons, principally benzene, naphthalene and anthracene along with acetylene, ethylene and other olefine by thermal decomposition of natural gas at temperature under 900° C. Silica was the best material for the heating tubes, while catalysts were of little value. Benzene yields up to 44 litres per thousand cubic meters were obtained, which these workers feel is about the limiting practical yield.

Stanley[109] has summarised the present uses of natural and cracking still gases, including their conversion into motor fuel.

The United States Bureau of Mines [110] is also studying the possibility of producing motor fuel by the cracking of natural gas.

The decomposition of methane or natural gas for the production of hydrogen or acetylene properly belongs to the gas-making art, and will not be considered in detail here. Papers on acetylene formation have been published by Peters and Meyer[111], Jones[112], and Fischer and Peters[113], while the method of the I.G. Farbenindustrie A.-G. is reported by Krauch[114], and other methods are discussed in a recent review.[115].

The decomposition of methane or natural gas to give hydrogen

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[106] *Nature*, 1928, **122**, 773.

[107] *Fuel*, 1928, **7**, 535. See also *Chaleur Ind.*, 1928, **9**, No. 102, 160.

[108] *Ind. Eng. Chem.*, 1929, **21**, 945.

[109] *J. Inst. Petr. Techn.*, 1929, **15**, 516.

[110] Bignell, *Oil Gas J.*, July 18, 1929, 39.

[111] *Brennstoff-Chem.*, 1929, **10**, 324.

[112] *J.C.S.* 1929, 419.

[113] *Brennstoff-Chem.*, 1929, **10**, 108.

[114] *Nat. Petr. News*, 1929, 69.

[115] *Petr. Times*, 1929, **21**, 650.

and carbon has been studied by Holliday and Exell[116], Kusama and Uno[117], Constable[118], Mantel,[119] and Yunker[120].

There has also been considerable activity in the study of the thermal decomposition of pure hydrocarbons without reference to the production of commercial products. Important papers have been published by Pease[121] on the decomposition of ethane, propane, butane, and iso-butane, Pease and Durgan[122] on ethane, Frey and Smith[123] on ethane, ethylene, propylene, and propane, Hague and Wheeler[124] on the normal paraffins from methane to hexane and acetylene and ethylene, and Hurd and Spence[125] on butane and isobutane.

UNITED STATES PATENTS.

G. Olivier (U.S.P. 1,677,363, July 17, 1928) claims

> "A process of converting methane gas into hydrocarbons of higher carbon content, consisting in gradually heating a thin stream of methane to a temperature not exceeding 950° C. which will form ethylene and ethylenic compounds, subjecting the products formed to a vacuum, and suddenly and completely cooling said products down to atmospheric temperature."

A. S. Ramage (U.S.P. 1,687,890, Oct. 16, 1928) presents a

> "Process of converting low boiling point hydrocarbons into higher boiling hydrocarbons which comprises mixing a hydrocarbon vapour similar to the lighter fractions of casing head gasoline with steam and contacting the resulting mixture with ferrous oxide at a temperature of at least 600° C."

H. A. Webster (U.S.P. 1,711,913, May 7, 1929) claims

> "In an apparatus for producing hydrocarbons and alcohol from natural gas the combination of a retort for decomposing said gas by heating; means for supplying a portion of said gas to said retort; a second retort adapted to be heated by the other portion of said gas; means for supplying the other portion of said gas to said second retort; means to supply steam alternately to said retorts; means to supply air alternately to said retorts and alternately with said steam supply; catalysing means communicating with said retorts; and means for conducting gas from said retorts to, through, and away from said catalysing means."

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[116] *J.C.S.* 1929, 1066.
[117] *Bull. Inst. Phys. Chem. Research (Tokyo)*, 1929, **8**, 1; *Abstr.*, 1929, **2**, 1.
[118] *Nature*, 1928, **122**, 882.
[119] *Przemysl Chem.*, 1928, **12**, 333.
[120] *Oil Gas J.*, May 9, 1929, 111. *Petr. Times*, 1929, **21**, 1160. *Gas Age-Record*, 1929, **63**, 673.
[121] *J. Amer. Chem. Soc.*, 1928, **50**, 1779.
[122] *J. Amer. Chem. Soc.*, 1928, **50**, 2715.
[123] *Ind. Eng. Chem.*, 1928, **20**, 948.
[124] *J. C. S.* 1929, 378.
[125] *J. Amer. Chem. Soc.*, 1929, **51**, 3353.

ENGLISH PATENTS.

ANGLO-PERSIAN OIL COMPANY. A. E. DUNSTAN and R. V. WHEELER (E.P. 309,455, June 6, 1929) report that

"Aromatic hydrocarbons, olefines, etc., are obtained by heat treatment of gases containing gaseous paraffins, *e.g.*, natural gases, gases from cracking plants, stills, low-temperature carbonisation retorts, etc. The gases are passed through a preheater at a temperature below that at which decomposition occurs, *e.g.*, below 550° C., and through reaction tubes or passages, wherein the gas is heated within a determined temperature range and for a determined time according to its composition. For example, the following temperature ranges are given for separate gases: Methane 850–975° C.; ethane 800—900° C.; propane 750—850° C.; butane 700—900° C. and pentane 650—750° C., the ranges being modified accordingly when mixtures of the above gases are treated."

F. FISCHER and H. PICHLER (E.P. 316,126, Sept. 18, 1929, not yet accepted) state that

"Aromatic and unsaturated hydrocarbons are prepared by heating methane to temperatures above 1000° C. for not more than one second."

P. H. HULL (E.P. 304,914, Mar. 27, 1929) proposes that

"Gaseous hydrocarbons be passed through an arc discharge between electrodes made of or coated with tungsten, molybdenum, osmium, tantalum, or compounds or alloys thereof. The carbides of these metals may be used. The electrodes may be clipped to water-cooled tubes and may diverge in the direction of the gas stream."

I. G. FARBENINDUSTRIE A.G. (E.P. 291,137, July 18, 1928) states that

"Liquid hydrocarbons of low boiling-point are obtained by passing olefines or gases containing them at elevated temperature and ordinary or increased pressure over catalysts comprising (1) gold, silver or copper in a coherent form, *e.g.*, as turnings or gauze or a lining to the reaction tube, (2) compounds, preferably oxygen containing compounds, of the alkali metals, to which may be added other metallic salts or oxides, (3) salts of the oxygen acids of phosphorus, boron or antimony, with alkali or other metals."

I. G. FARBENINDUSTRIE A.G. (E.P. 296,034, Oct. 17, 1928) arranges that

"Coal, tars, mineral oils, bitumens, coal extraction products, hydrogenation products of coal, oil schists, etc., are atomised and heated with steam to produce a pyrogenic decomposition giving gases rich in olefines, which are then heated with or without pressure and with or without catalysts so as to produce liquid hydrocarbons of low boiling point, which may be in part aromatic. During the second stage it is necessary to avoid the contact of the gases with iron or the like which cause the deposition of soot; the apparatus employed may be lined with copper, silica, ferrosilicon, etc. The catalysts employed in the second stage of the process may be metal oxides, silica, graphite, active charcoal, mica, pumice, porcelain, barium carbonate, a barium salt deposited upon carbon, and copper, silver, gold, chromium, boron or their compounds."

I. G. FARBENINDUSTRIE A.G. (E.P. 299,086, Dec. 12, 1928) obtains oils of high viscosity and flash-point

"By passing gases, rich in lower olefines, *e.g.*, ethylene, propylene, butylene and amylene, which may be obtained by cracking tar or mineral oils, or as a by-product from other industrial processes, into hydrocarbon mixtures which are liquid at ordinary temperatures, in the presence of catalysts of the Friedel-Crafts type, *e.g.*, the chlorides of aluminium, zinc or trivalent iron."

I. G. FARBENINDUSTRIE A.G. (E.P. 303,998, Mar. 6, 1929) claims that

"Olefines and diolefines are obtained by catalytic treatment in a vaporous state of paraffins, olefines or mixtures thereof, which may be cyclic, at temperatures between 500—800° C., using as catalyst lustrous carbon (Glanzkohle) which is deposited from hydrocarbons at temperatures above 650° C. It may advantageously be employed on carriers, such as difficult reducible metal oxides and compounds or mixtures thereof as employed in the process of Specification 297,398, such as glucinum oxide, tertiary calcium phosphate, and other bodies such as alumina, chromium oxide, active silica, natural or artificial silicates, quartz, porcelain or on metals, like copper, chromium, etc."

I. G. FARBENINDUSTRIE A.G. (E.P. 309,199, May 29, 1929) produces

"Liquid hydrocarbons by passing olefines or gases containing them in contact with metals in a coherent state such as iron or copper superficially coated by a process involving heating, with tin, zinc, aluminium, or chromium at any suitable pressure and high temperature."

I. G. FARBENINDUSTRIE A.G. (E.P. 311,899, July 10, 1929) states that

"Liquid hydrocarbons, especially of the aromatic series, are obtained by passing methane, ethane or mixtures thereof, together with unsaturated hydrocarbons, especially olefines, or with higher homologues of the paraffin series, if desired, together with hydrogen, at temperatures preferably between 500° and 900° C. over specified catalysts. The catalysts specified are carbonates of the alkaline earths, carbonates and salts of magnesium and beryllium, alone or admixed, or mixtures thereof with compounds of other metals, particularly salts of the alkaline earth metals, or in place of the salts of magnesium and beryllium, the oxides and hydroxides thereof. Further, compounds of selenium, tellurium or thallium, active charcoal, active silica, pumice stone, lustrous carbon, metallic aluminium, sodium borate, aluminium borate, barium carbonate precipated on diatomaceous earth or porous carbon, or barium oxide may be used as catalysts."

G. C. LEWIS (E.P. 309,488, June 6, 1929, not yet accepted) obtained hydrocarbons and free carbon

"From natural gas or similar hydrocarbon containing gases by heating the gas to a temperature at which cyclic hydrocarbons are formed, but below that temperature at which free carbon appears, removing any condensable products, and causing the residual gas to undergo incomplete combustion."

8.—Gases Produced by Cracking.

Gas from the cracking process has attained a position of considerable commercial importance. Egloff[126] states that 250 billion cubic feet of cracked gas was produced in the United States during 1928. The gas is high in unsaturated compounds, which gives it its distinctive value. In addition to serving as refinery fuel, this gas is finding employment for enriching gas of lower fuel value, such as water gas, and in chemical synthesis, particularly in the manufacture of alcohols, acetone, and glycol.

Considerable attention has been paid, particularly in the patent literature, to controlling the cracking process for high production of olefines and diolefines, especially butadiene.

Wagner [127] states of vapour phase cracking, "it has been discovered that over half of the dry gas can be converted into motor distillate of even higher anti-knock properties than the original product of the vapour phase cracking operation."

Markowitch[128] describes the cracking and rectification of cracked products of a Russian blau gas plant producing a gas containing 64 per cent. of unsaturates by weight, and a liquid product reported to contain 22 per cent. of butadiene in a total unsaturated content of 92 per cent.

Pilat and Winkler [129] found the optimum temperature for the formation of olefines, convertible to secondary alcohols, by cracking gas oil in the vapour phase, to be between 600 and 670° C.

Dobryanskii, Arkhangelskii and Stepanyan[130] cracked a number of oils by passing them through a copper tube at 550 to 750° C. in order to obtain propylene. Solar oil at 600 to 650° C. gave the optimum yield of 13 per cent. At higher temperature the propylene decomposed and ethylene increased. In cracking gasoline five times a yield of 23 per cent. by weight of propylene was obtained.

9.—Treating of Cracked Distillates.

Much has been written of the use of hypochlorite in treating cracked oils. Dunstan and Thole[131] stated that at first the use of hypochlorite was unsuccessful with cracked distillates because of the chlorination it produced. It has been found however, that the chlorination can be avoided by regulating the alkalinity. Hypochlorite will sweeten, but not thoroughly desulphurise

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[126] *J. Amer. Chem. Soc.*, Minneapolis Meeting, Sept. 9-13, 1929.
[127] *Nat. Petr. News*, Oct. 30, 1929, 173. *Oil Gas J.*, Oct. 31, 1929, 46.
[128] *Neftyanoe Khoz.*, 1929, **16**, 67.
[129] *Przemysl Chem.*, 1929, **13**, 185.
[130] *Neftyanoe Khoz.*, 1928, **14**, 46.
[131] *Oil Gas J.*, May 23, 1929, 190. See also Dunstan, *Oil Gas J.*, Dec. 13, 1928, 138.

cracked oils, and must be followed by some treatment such as use of fuller's earth to remove gum forming bodies.

Birch and Norris[132] also discuss the hypochlorite refining of cracked distillates, and state that the action of this agent is analogous to the use of sodium plumbite and elementary sulphur, but avoids the risk of free sulphur finding its way into the finished product. The hypochlorite process is stated to be effected at lower cost than plumbite treatment, to lessen the loss of aromatic and unsaturated hydrocarbons, and to give rise to no objectionable slude. Birch[133] gives as a treating procedure, washing with soda to remove hydrogen sulphide, sweetening with hypochlorite, acid treatment, washing with soda and re-running. The hypochlorite may also be applied after re-distillation.

Birch and Norris,[134] in discussing the chemical reactions taking place when petroleum fractions, particularly light oils, are chemically refined, also consider the polymerising action of sulphuric acid and of fuller's earth on cracked distillates.

Hewetson[135] shows that the desulphurising of West Texas cracked distillate presents a difficult problem. A number of treating methods possible in the laboratory, such as use of mercuric acetate, are too costly for plant use. Acid treatment appears the most practicable treating means, with due regard to strength of acid, temperature and time of contact. Other acids are more expensive and less desirable. An excess of hypochlorite or a too concentrated solution tends to produce chlorination, while its use before acid treatment tends to reduce sulphur, but the same result may be obtained at less expense by using more acid.

Experiments in treating in the vapour phase with fuller's earth, bauxite, pumice wet with phosphoric acid, and oxides of calcium, cadmium, and aluminium, in towers connected with distillation, or in tubes at 600°–1000° F. sometimes sweetened the gasoline, but in no case reduced the sulphur-content appreciably.

Mercuric and copper chlorides were valueless, while chlorides of aluminium, antimony, bismuth, iron, tin, and titanium would in general sweeten the gasoline but failed to decrease the sulphur content of the oil.

Hounsell[136] draws attention to the loss by vaporisation and harm from oxidation during air blowing of cracked distillates in acid treating. He advises continuous treatment of cracked distillates

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[132] *Ref. and Nat. Gas. Mfr.*, July, 1928, 94.
[133] *Oil Gas J.*, May 30, 1929, 38.
[134] *Trans. Fuel Conference, World Power Conference, London*, 1928, **1**, 641; *Oil Gas J.*, July 11, 1928, 46.
[135] *Bull. Amer. Petr. Inst.*, 1929, **10**, No. 2, Sect. 2, 79.
[136] *Oil Gas J.*, June 7 ,1928, 201.

with 62–64° Be. (84 per cent.) sulphuric acid, which acts on diolefines but does not remove aromatics and simple olefines. The acid treatment is followed by doctor, and after re-running by a small amount of caustic.

Yost[137] describes the equipment used by the Pure Oil Co. for sweetening and acid treating of cracked and other light distillates. In the acid treatment, acid and pressure distillate are mixed in a centrifugal pump, passed through an orifice column, through settlers to remove the sludge and apparatus for water and caustic washing. From 0·7 to 1·2 lb. of acid per barrel of oil are used.

Reid[138] describes the continuous acid treating process applied by the Indian Refining Company to freshly cracked gasoline. Morrell and Bergman[139] present a number of designs of equipment for the batch and continuous treatment of light oils, including cracked distillates.

Hounsell[140] describes the refining of a high sulphur Dubbs pressure distillate from Smackover crude, which is washed with water to eliminate most of the hydrogen sulphide, acid treated, washed, brought in contact with a solution of copper ammonium hydroxide (blue solution) and then is redistilled to motor fuel. Treatment with a large quantity of sulphuric acid of high concentration is avoided in order to preserve the unsaturated compounds present in the oil. The finished gasoline is reported to be sweet and of high anti-knock value, a result which could not be obtained by the treatment with acid, hypochlorite, and doctor solution alone.

Wilson[141] states that at the Simms Oil Company Refinery in Dallas, Texas cracked gasoline is washed with caustic soda, settled, acid treated, the tar separated in a centrifuge, the oil then agitated with 3 lbs. of fine clay (200 mesh) per barrel, and freed from the clay in a Sweetland press. The resultant gasoline is said to be completely colour-stable.

Chatfield[142] reports that the trend in Gray vapour phase treatment is apparently to give a slight acid treat before charging to the towers.

Gerstenberger[143] states that heavy dark coloured naphtha may be much improved in quality by treatment with soap solution. Voorhees and Eisinger[144] criticize the gum tests in common use and point out the particularly unsatisfactory nature of the copper

[137] *Oil Gas J.*, Aug. 23, 1928, 120; Nov. 15, 1928, 172.
[138] *Ref. and Nat. Gas. Mfr.*, Jan., 1929, 60.
[139] *Chem. Met. Eng.*, 1928, **35**, 210, 291, 350.
[140] *Oil Gas J.*, Mar. 14, 1929, 31.
[141] *Oil Gas J.*, Aug. 16, 1928, 130.
[142] *Nat. Petr. News*, June 13, 1928, 25.
[143] *Nat. Petr. News*, Feb. 20, 1929, 61.
[144] *Oil Gas J.*, **27**, No. 31, 152. (1928).

dish test. They recommend evaporating gasoline in an atmosphere of steam for determination of the gum content and use of an oxygen test to determine stability and potential gum formation.

UNITED STATES PATENTS.

J. C. BLACK (U.S.P. 1,696,377, Dec. 25, 1928) presents a process

"Which comprises treating with cadmium hydroxide suspended in an aqueous solution in quantities sufficient to combine with sulphur bearing constituents to be separated, combining the same therein, and separating the treated hydrocarbons from the sulphur bearing constituents combined with the said cadmium hydroxide."

"As a specific example, in the treatment of gasoline stocks derived from cracking California petroleum oil distillates, it was found that the amount of cadmium hydroxide necessary to move all the mercaptans, hydrogen sulphide, and free sulphur present ranged from ¼ to 1½ pounds, calculated to cadmium oxide, per barrel of gasoline stock treated, the cadmium hydroxide being formed by adding to a water solution of cadmium chloride or sulphate, an excess of a water solution of caustic soda, so that all the cadmium was converted into cadmium hydroxide and remained suspended in the caustic alkaline water solution."

J. C. BLACK (U.S.P. 1,710,200, Apr. 23, 1929) claims

"A process of treating hydrocarbon oils with sulphuric acid in the presence of liquid sulphur dioxide which comprises commingling the hydrocarbon oil containing added liquid sulphur dioxide with the requisite amount of sulphuric acid, and then separating the products of reaction, sulphur dioxide and the uncombined acid from the treated oil."

"For example, in the treatment of a gasoline stock, made by cracking a petroleum oil distillate at a pressure of approximately 1,000 pounds gauge, by our process approximately 5 to 10 pounds of 3 per cent. fuming sulphuric acid was required to obtain a stable water white gasoline product with a treating loss ranging from 1 to 4 per cent. by volume; while by the employment of well-known methods of acid treating a loss of from 2 to 6 per cent. by volume was obtained employing the same quantities of acid."

H. BLUMENBERG, JR. (U.S.P. 1,700,347, Jan. 29, 1929) covers a process of treating mineral oil and its products including cracked distillates

"With hydrochloric acid and decomposing said hydrochloric acid electrolytically in the presence of aluminum.

"A process of treating mineral oil and its products comprising adding from 2 to 7 per cent. by weight of hydrochloric acid to the mineral oil distillation product, disposing electrodes within the liquid, the anode being made of aluminum, passing an electric current through the liquid and said electrodes."

H. BLUMENBERG, JR. (U.S.P. 1,716,103, June 4, 1929) claims a process of refining, comprising treating the oil

"With a sulphite of aluminum, heating the mixture to a temperature of 160°F., and distilling off the volatile constituents."

W. N. Davis, W. H. Hampton and E. N. Klemgard (U.S.P. 1,705,809, Mar. 19, 1929) present

"In a process of treating cracked petroleum naphtha and similar high sulphur petroleum distillates with sulphuric acid to remove sulphur bodies, substantially reducing the polymerisation of unsulphured bodies by treating the oil at below 38°F. with an acid of lower freezing point than the reaction temperature."

"The temperature found most favourable for the cold treatment is between 15 and 20°F."

T. G. Delbridge and J. B. Hill (U.S.P. 1,682,603, Aug. 28, 1928) presents for refining cracked petroleum distillates

"The method which comprises fractionating the vapours of the distillate by contact with reflux liquid, condensing the vapours, bringing the condensate in liquid phase at a temperature substantially above its normal boiling point into contact with fuller's earth to effect polymerization of gum-forming and colour-imparting bodies, maintaining thereon while in contact with the fuller's earth a super-atmospheric pressure of such magnitude as to maintain the oil in liquid phase, transporting polymers from the fuller's earth by the oil, thereafter distilling the treated oil to effect separation of lower boiling point vapours from higher boiling point oil containing the polymers in solution, and utilising said higher boiling oil as reflux liquid in said fractionation."

G. Egloff (U.S.P. 1,703,616, Feb. 26, 1929) discloses

"A process for treating cracked distillates to remove sulphur compounds therefrom comprising commingling with the cracked distillates a quantity of a drying oil, subjecting the resulting mixture to a temperature sufficiently high to cause a rapid combination between the drying oil and the sulphur compounds, subjecting the mixture to distillation under a super-atmospheric pressure and recovering the overhead product formed during such distillation."

G. Egloff and J. C. Morrell (U.S.P. 1,725,068, Aug. 29, 1929) claims

"A step in a process for treating cracked products containing sulphur compounds, comprising agitating the oil in the presence of copper sulphate in sulphuric acid solution."

H. J. Halle (U.S.P. 1,681,638, Aug. 21, 1928) has invented

"A refining process consisting in passing oil vapours through a column of heated sulphuric acid maintained at a temperature at least equal to the temperature of the oil vapours, said acid being in excess of concentration of 20 per cent. and not exceeding 55 per cent, and in subjecting the vapours of said acid treatment to a neutralising treatment to produce gasoline."

R. A. Halloran (U.S.P. 1,704,246, March 5, 1929) presents

"The process of treating petroleum oil pressure distillate having a sulphur content in excess of two-tenths of one per cent, which consists in washing the same with water directly after condensation thereof without releasing the distillate from the degree of pressure reduction requisite for the evolution of the wet gases from the pressure distillate and then without substantial release of said pressure contacting the same with a solution of alkali."

L. M. JOHNSTON (U.S.P. 1,706,614, March 26, 1929) outlines a

"Method of treating hydrocarbon oil which includes forming a treating medium into a paste or mud, forming the paste into strings and permitting the same to accumulate to form a porous column of treating medium, vapourising the hydrocarbon oil and passing the vapours through said column to be treated thereby and out through the top thereof."

V. A. KALICHEVSKY (U.S.P. 1,695,251, Dec. 11, 1928) has devised a process for the purification of petroleum distillates containing difficulty adsorbable colouring matters, applicable to cracked gasoline

"Comprising subjecting the stock to a caustic wash sufficient to convert colouring matters into adsorbable forms, then subjecting the distillate to the action of acid and clay to absorb the converted constituents, and removing the clay from the distillate to yield a final product."

A. LACHMAN (U.S.P. 1,709,315, Apr. 16, 1929) patents

"A method of refining mineral oils which consists in heating the oil to form a vapour, passing the heated vapour through or in contact with a body of phosphoric acid maintained under high concentration, maintaining the acid at such concentration by the continuous addition of water and condensing the vapour after passing through the fluid acid."

M. LUTHER and K. PIEROH (U.S.P. 1,732,371, Oct. 22, 1929) covers

"The process of purifying products of the destructive hydrogenation of carbonaceous materials, which consists in treating same with a formate of a lower aliphatic alcohol as an extraction liquid and separating the solution of formate containing the impurities from the purified oils."

In an example

"A distillate from Mexican crude oil is shaken up several times with its own volume of methyl formate. The resulting oil is light in colour, no longer turns dark afterwards, and is entirely free from the unpleasant smell attaching to the original product. The sulphur content is reduced from 2·3 per cent. to 0·6 per cent."

P. MCMICHAEL (U.S.P. 1,669,944, May 15, 1928) has invented

"A method of refining petroleum oils and distillates which comprises subjecting the oil to treatment with sodium hyposulphite and a heavy metal compound in alkaline aqueous solution, and thereafter subjecting the treated oil to treatment with a dilute aqueous solution containing a free acidic constituent."

E. B. MILLER (U.S.P. 1,678,299, July 24, 1928) arranges

"In a cyclic apparatus for refining liquids, in combination, an agitating device adapted to contain a hard porous adsorbent material, means to supply liquid to be refined to said device, a separator connected to said agitating device wherein the liquid and the material are separated, an activator, means to convey the separated material from said separator to said activator, a second separator to separate the adsorbing material and vapours after their discharge from said activator, and means to return the activated material from said last-mentioned separating means to said agitating device."

Cf. PATRICK and MILLER (U.S.P.) 1,678,298

J. C. MORRELL (U.S.P. 1,7100,063, Apr. 23, 1929) offers

"A process for refining hydrocarbon oil comprising removing a portion of the sulphur content by subjecting the oil to treatment with plumbite solution, removing said solution and distilling the oil, combining the recovered distillate with refined residual oil from a previous distillation to form a mixture in which the residual oil is in excess of 50 per cent., and subjecting the mixture to a redistillation."

J. C. MORRELL (U.S.P. 1,733,619, Oct. 29, 1929) presents

"A step in a process for refining the lighter gravity liquid products obtained from the distillation or cracking of petroleum oils, comprising subjecting said lighter gravity liquid products to the action of an acid sulphate in aqueous solution."

A. OBERLE (U.S.P. 1,674,020, June 19, 1928) claims

"A process for decolorising and purifying petroleum hydrocarbons, consisting in contacting the oil with a treating solution containing potassium iodide, permitting the oil and treating solutions to separate, and separating the treated oil from the treating material by filtration."

W. A. PATRICK (U.S.P. 1,678,298, July 24, 1928) introduces

"In the process of refining oils, the step consisting in treating the oil with a solid absorbent material having pores of such size that it will adsorb water vapour to such an extent as to contain not less than about 10 per cent. of its own weight of water when in equilibrium with water vapour at 30°C. and a partial pressure of substantially 22 mm. of mercury."

Silica gel is the preferred adsorbent.

"In cases where silica gel is not suitable, other gels or adsorbing materials may be used, provided they have a sufficient number of small pores as defined above, *i.e.*, activated charcoal, gels of iron oxide, tin oxide, aluminium oxide, tungstic oxide, zirconium oxide, and titanium oxide."

E. A. PRUDHOMME (U.S.P. 1,674,796, June 26, 1928) has invented a process for the treatment of hydrocarbon products, including cracked distillates "which consists in vaporising said products at a temperature less than 400°C., and in passing all of the products of evaporation at a temperature above 180°C. first through a purifying element containing a metallic oxide and then through catalysing elements containing a metallic base, and finally through activated carbon with the addition of a reducing gas without further heating."

Nickel suboxide, and oxides of copper, vanadium and cobalt are mentioned as catalysts.

H. ROSTIN (U.S.P. 1,732,111, Oct. 15, 1929) covers a process of hydrogenating carbon containing compounds that is applicable to cracked gasoline

"Which comprises conducting the compounds together with sulphuretted hydrogen over finely divided iron at a temperature sufficiently high to cause the release of nascent hydrogen and the reaction of the released hydrogen with the compound."

ENGLISH PATENTS.

C. Arnold (E.P. 305,108, March 27, 1929) purifies vapours of hydrocarbon oils, particularly naphtha or gasoline produced by cracking processes, by passage

"Countercurrent to a stream of liquid carrying a finely divided solid adsorbent or absorbent, such as clay, at a temperature such that the required vapours pass on."

Galicyjskie Towarzystwo Naftowe Galicja Soc. Anon., W. De Piotrowski, and J. Winkler (E.P. 309,718, June 6, 1929) disclose a process in which

"Acid tars resulting from the refining of benzine or other products obtained by cracking processes are diluted with water and alkaline liquor, such as those which have been used for washing the acid-refined benzene. An upper oily layer separates out. The lower aqueous layer is neutralised and distilled with superheated steam yielding a distillate containing butyl, amyl, hexyl, &c. alcohols which may be used for denaturing ethyl alcohol. The oily layer is neutralized, dried and distilled with steam. The fraction collected between 50—200°C. is refined with caustic lye and sodium plumbite to form an insecticide. The fraction collected between 200—280°C. is heated with manganese or cobalt driers to form varnish-like products or is polymerised to yield substances of higher molecular weight.

Gray Processes Corporation (E. P. 293,440, Aug. 29, 1928, not yet accepted) purifies fluids such as hydrocarbon distillates

"By passing them preferably vaporised through solid adsorptive material such as fuller's earth, which is revivified at intervals by materially reducing the pressure applied to the effluent fluid below that applied to the entering fluid."

G. Petroff (E.P. 289,561, June 20, 1928) deodorises naphtha distillates, petroleum, cracked oils, and oils obtained by the dry distillation of bituminous fossils

"By passing air or other gas containing free oxygen through a series of vessels containing free oxygen through a series of vessels containing the oil, heavy metal salts of fatty, naphthenic, or resin acids being dissolved in the oil in the first vessel, and metal turnings or power being present in the others. Such salts of lead, manganese, cobalt, copper, zinc, iron, calcium, and chromium are specified."

H. Rostin (E. P. 286,255, April 25, 1928) provides that

"Liquid and gaseous hydrocarbons, *e.g.*, oils, the products of cracking or destructive distillation, and water gas are hydrogenated and purified by passage with sulphuretted hydrogen over iron, preferably finely divided and freshly reduced . . . Cracked oils or crude benzole are vaporised, mixed with sulphuretted hydrogen, and similarly treated."

W. H. Smith (E. P. 288, 193, May 31, 1928, not yet accepted) presents a process in which

"Oils are cracked and ores, especially iron ore, simultaneously reduced by passing the oils through a series of heated closed chambers or retorts through which a stream of ore is continuously fed. The retorts are preferably heated by electric resistances to control the temperatures accur-

ately. The iron ore acts as a catalytic agent but the retort walls may also be lined with catalysts, or catalysts, *e.g.*, chromium, nickel, magnetite, reduced iron sponge, may be mixed with the ore."

STANDARD OIL COMPANY OF CALIFORNIA (E.P. 301,450, Jan. 23, 1929, not yet accepted) states that

"The polymerisation loss of unsaturated sulphur-free hydrocarbons during the desulphurisation of motor fuel, particularly cracked naphthas, by treatment with sulphuric acid is controlled by limiting the maximum reaction temperature of the fuel and acid. This can be effected by cooling the mixture during the reaction, by cooling the oil before mixing with the acid, or by a combination of the two methods; in the case of an oil of high sulphur-content, the necessary acid can be added in small increments, and the heat resulting from each addition absorbed separately. The reaction temperature is preferably kept within 15°F. of the initial temperature and the maximum is preferably between 5 and 40°F."

F. B. THOLE, S. F. BIRCH, and W. S. G. P. NORRIS (E.P. 288,931, June 13, 1928) provide that

"In the refining of petroleum, kerosine, or benzine by alkaline solutions of alkali or alkaline earth hypochlorite, the concentration of the free alkali is not substantially less than 1·5 per cent. whereby the evil-smelling sulphur compounds are converted into others less offensive adapted to be removed with the remaining sulphur compounds by subsequent refining treatment."

S. TIJMSTRA (E.P. 318,706, Oct. 30, 1929) desulphurises cracked and other hydrocarbon oils

"By treating with alkaline plumbite, separating, preferably washing with water, and then treating with an aqueous solution of polysulphide advantageously at 80-90°F."

PATENTS OF OTHER COUNTRIES.

F. R. MOSER (Australian P. 15,631, July 9, 1929) reports

"A process for refining petroleum or petroleum products (including cracked products), as well as the extracts obtained therefrom, in known manner with liquid sulphur dioxide by means of acids, wherein the originating materials are in the first stage subjected to treatment with dilute acid of a strength which will not form acid sludge for the purpose of removing the basic substances therefrom, and in a second stage with concentrated acid to effect the refining proper."

W. G. LEAMON (Can. P. 292,692, Sept. 3, 1929) claims a

"Process of producing a stabilised petroleum product which comprises subjecting a cracked petroleum distillate having a specific gravity of between 0·730 and 0·830 to the action of a metallic halide having a polymerising action on gum-forming constituents in said distillate, said metallic halide being dissolved in an ether, and separating resultant gummy products from the liquid."

N.V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ (Fr. P. 658,639, Aug. 6, 1928) refines petroleum and petroleum products including those formed by cracking, in two stages, first with dilute acid and then with acid of the usual strength.

HERBERT WITTEK (D.R.P. 466,264, Oct. 1, 1928) claims

> "A process by which cracked distillate or coal hydrogenation products boiling at 30-150°C. are diluted with benzine, treated with one per cent. by weight of concentrated sulphuric acid, washed, and the acid-free oil distilled to give motor benzine."

10.—GENERAL REVIEWS.

Burgart and Graetz[145] review the history of cracking, the different methods now used and the influence of catalysts. Hurd[146] briefly discusses cracking in its relation to the larger field of the pyrolysis of carbon compounds. Heller[147] discusses the present status of cracking. Koudelak[148] reviews the commercial cracking process in current use. Magnus[149] outlines the development of cracking in Germany with particular reference to the patent situation. Sachs[150] presents a review of the literature on cracking. Seduikh[151] and Auld[152] review methods of cracking in the vapour phase. Singer in discussing advances in petroleum distillation in the last ten years, takes up several cracking processes[153], and also contributes a summary[154] of recent publications concerning cracking.

Patents covering cracking and hydrogeneration are reviewed by Pincass[155] and Naphthali[156].

Graetz[157] takes up present tendencies in the cracking industry with particular reference to the thermal reactions of individual hydrocarbons.

Dunstan and Pitkethly[158] outline the progress made in cracking in the last ten years, and discuss in detail several processes now in use. Ormandy[159] contributes a general discussion of cracking and hydrogenation.

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[145] *Tech. moderne*, 1928, **20**, 377.
[146] "Pyrolysis of the Carbon Compounds," Chemical Catalog Co., N.Y., 1929.
[147] *Z. Ver. deut. Ing.*, 1928, **72**, 335.
[148] *Paliva a Topeni*, 1928, **10**, 36, 51, 67, 89, 109, 119.
[149] *Erdöl u Teer*, 1929, **5**, 207.
[150] *Chem. Ztg.*, 1929, **53**, 65, 86, 107, 147. See also Parsons, *Chem. Ztg.* 1929, **53**, 167.
[151] *Neftyanoe Khoz.*, 1928, **15**, 677.
[152] *Petr. Times*, 1929, **21**, 99, 158.
[153] *Oesterr. Chem. Ztg.*, 1928, **32**, 1. See also *Metallbörse*, 1928, **18**, 901, 1014, 1071.
[154] *Petroleum Z.*, 1928, **24**, 175; 1929, **25**, 741, 849, 986, 1025, 1051, 1216 1316.
[155] *Petr. Times*, 1928, **20**, 1020.
[156] *Petroleum Z.*, 1928, **24**, 611.
[157] *Ann. Office Nat. Combustibles Liquides*, 1928, **3**, 779.
[158] *Trans. Fuel Conference, World Power Conference, London*, 1928, I, 693. *Petr. Times*, 1928, **20**, 719.
[159] *J. Inst. Fuel*, 1929, **2**, 199.

Egloff[160] emphasises the great importance of the cracking process in connection with the future need for gasoline, estimating that motor fuel must be supplied for about 75 million cars by 1938.

Wilson[161] outlines the 15 years history of the Burton process while Naphthali[162] reviews the operation of commercial cracking processes and Owen[163] discusses the development of the cracking art.

11.—Magnitude of the Cracking Industry.

On January 1, 1929, there were 2,205 cracking units completed or being built in the United States, with a total daily charging capacity of 1,476,874 barrels. A year earlier there had been 2,334 units with a total capacity of 1,288,000 barrels, indicating an increase in capacity of nearly 200,000 barrels.

"In common with most other kinds of industrial equipment, the average size of cracking units has considerably increased.[164] This fact was particularly well illustrated by this survey, which, in comparison with the 1928 survey, showed an increase in size of the average unit of from 552 barrels daily charging capacity to 670 barrels. Five years ago the majority of the new units projected were of 500 barrels daily charging capacity, but to-day it is not uncommon for units of 3,000 or 4,000 barrels capacity to be built."

The cracking capacity of refineries outside the United States is estimated at 200,000 barrels per day.

The recent production of gasoline by cracking and other methods in the United States is shown by the figures below :—

Production of Gasoline, 1927-1929, in Barrels.

	1929 (estimated).	%	1928[165].	%	1927[166].	%
Total gasoline (exclusive of benzol)	425,000,000		376,945,000		330,667,000	
Straight run gasoline	242,500,000	57·0	219,168,000	58·1	197,282,000	59·7
Cracked gasoline	140,000,000	33·0	122,554,000	32·5	101,224,000	30·6
Natural gasoline	42,500,000	10·0	35,223,000	9·4	32,161,000	9·7

[160] *Nat. Petr. News*, Nov. 21, 1928, 88.
[161] *Ind. Eng. Chem.*, 1928, **20**, 1099.
[162] *Brennstoff-Chem.*, 1929, **10**, 170. *Auto-Technik*, Mar. 3, 1929, 8.
[163] *Chem. Met. Eng.*, 1928, **35**, 677, 737.
[164] *U.S. Bureau Mines Circ.* **6127**, May, 1929.
[165] Annual Petroleum Statement, U.S. Bureau of Mines.
[166] *Oil Gas J.*, Mar. 1, 1928, 120, from U.S. Bureau of Mines.

Anti-Detonators.*

By W. H. Coleman, M.I.Min.E., F.I.C. (Member).

The two years 1928 and 1929 have been fertile in general work on the action of anti-detonators and on the causes of detonation (or pinking) in internal combustion engines, but reviewing the work together it still appears that we do not yet know exactly what detonation is or is due to, nor exactly how anti-knock dopes act when added to the fuel. It is true that many theories as to what detonation is and to what it is due have been put forward, but until we know a good deal more about the mechanism of combustion as it takes place in the cylinder of an internal combustion engine we are only able to attempt to get over the trouble empirically.

Perhaps the work that may throw the most light on the problem of detonation is that concerned with the study of explosions in tubes and cylinders, and in this connection reference may be made to the work of Maxwell and Wheeler[1]. Among other useful matter these workers have confirmed the suggestion made by Egerton and Gates that the suppression of detonation by metallic dopes such as lead tetraethyl and iron and nickel carbonyls is due to the finely divided metal or metallic oxide resulting from the thermal decomposition of the dopes rather than to any action of the dopes as such.

Ellis and Kirby and Wheeler have also done good work on flame movements which one may hope will lead to an understanding of what detonation really is.

An interesting résumé on the "History and Development of Anti-detonating Agents" was read by H. S. Tegner before the Institute of Fuel.

A considerable amount of matter has been published by W. A. Whatmough dealing with this subject. Another aspect of the question which has received considerable attention is that of determining what may be described as the knocking or pinking tendency of different fuels. Perhaps the most interesting and exhaustive work published is that of Messrs. Stansfield and Thole[2].

* Paper received February 5, 1930.

[1] *J. Inst. Petr. Techn.*, 1928, **14**, 175; 1929, **15**, 408.

[2] *Ind. Eng. Chem.*, 1929.

These workers have outlined the methods of testing with several different variable compression engines and have described a new type of testing engine which they have designed and in which the bouncing-pin method of Midgley is combined with a variable compression arrangement and which they claim to give very satisfactory results. G. C. Brown[3] discusses the methods used for rating the anti-knock value of fuels, and finds that the point of incipient pinking is satisfactory but that the point of maximum power is not so satisfactory.

E. A. Watson[4], in a paper on "The Electrical Condition of Spark Gaps and Sparking Plugs" found that the voltage necessary to cause the spark to jump the gap decreased after pinking had set in and suggested that the measurement of the voltage might be adapted to determine detonation.

King and Moss[5] compare various methods of ascertaining the anti-knock value of motor fuels and point out that the effect of the addition of lead tetraethyl rises to a maximum and then falls off, whereas the reverse is the case with such bodies as benzene which, however, have to be added in very much greater proportion. They give tables showing that the cost of adding an anti-knock material may exceed the value of the gain in efficiency.

G. Edgar[6] submitted samples of five different fuels to nine laboratories for examination as to their anti-knock value with the following results:—

Three laboratories using the bouncing-pin method agreed with an error of ± 10 per cent.

Three laboratories using methods depending on variable throttle opening agreed with an error of ± 40 per cent.

Three laboratories using audibility methods agreed with an error of ± 60 per cent.

The divergencies were attributed to variations in the air fuel ratio.

The auto-ignition temperatures of various hydrocarbons have some bearing on their detonating tendency and this subject has been studied by Messrs. Masson and Hamilton[7].

Dr. E. W. J. Mardles[8] describes some interesting work on the effect of the addition of various bodies on the formation of active

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[3] *Oil and Gas J.*, 1929, **41**, 156.
[4] *Proc. Inst. Auto. Eng.*, **22**, 426.
[5] *Engineering*, 1929, **128**, 219-221, 272-274.
[6] *J. Soc. Aut. Eng.*, 1928, **28**, 41.
[7] *Ind. Eng. Chem.*, 1929, **21**, 544-549.
[8] *J.C.S.*, 1928.

oxygen when hexane air mixtures are passed through tubes heated to various temperatures and also the effects of water and 60 per cent. hydrogen peroxide spray on auto-ignition temperatures, and found that both water and hydrogen peroxide raised the auto-ignition temperature. He also gives figures showing the influence of various knock inducers in lowering the spontaneous ignition temperature.

A. C. Egerton[9] describes work on the rise of auto-ignition temperatures due to the addition of the vapour of metals dispersed by the electric arc decomposition of various metallic compounds. Knock-ratings and benzole equivalent values of various straight run, cracked and blended American gasolines are given in the *Oil and Gas Journal*, Vol. 26, 39, 140.

Dumanois and Mondain-Monval[10] have studied combustion with and without lead tetraethyl. They give curves showing how a very small percentage of the anti-knock compound steadies the heat pressure curve of pentane-air mixtures but has no effect on benzene-air mixtures.

A discussion on the nature of detonation is reported[11], and Wawrzinick[12] describes experiments showing that the addition of ethyl ether to any fuel causes pinking and states that the addition of paraffin or water by spraying from a special carburettor eliminates all tendency to pink. The author suggests that the heat absorbed by these added components prevents the initiation of the detonation wave. He states that as much as 90 per cent. of water could be added to the fuel without reducing its efficiency. Y. Nagai[13] describes experiments on the influence of the addition of small amounts of diethyl-selenide, tetra-methyl tin and tetra-methyl lead on the speed of flame movement in hydrocarbon air mixtures and finds that up to a certain small percentage the retarding effect increased, but that the rate of increase fell off as the amount of dope added was increased.

A considerable number of suggestions for decreasing or suppressing detonation have been put forward, among which may be mentioned the following.

Bloxham[14] distils gasoline up to 160°C. and treats the residue with liquid sulphur dioxide, separates the portion soluble in liquid

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[9] *Nature* (Supplement), 1928, **122**, 3062.
[10] *Compt. rend.*, 1928, **187**, 892.
[11] *J. Soc. Aut. Eng.*, 1928, **22**, 530.
[12] *Auto-Technik.*, 1928, **17**, 17-21.
[13] *Proc. Imp. Acad. Tokyo*, 1928, **4**, 525.
[14] E.P. 295,253.

sulphur dioxide and adds it to the lower fraction thereby producing afuel with anti-knock properties.

Gebüder Avenarius (Berlin) and H. D. Elkington[15] claim the addition of 0·3 to 0·5 per cent. of the esters of the higher molecular weight fatty acids to stop pinking.

H. D. Elkington[16] claims the use of a solution or dispersion of any anti-knock dope whether soluble in motor fuel or not, and gives as an example the use of potassium gallate dispersed in benzine so that each litre of fuel contains 1 gramme of potassium.

Egerton and Barton[17] claim the addition of a petrol soluble compound of an alkali metal, *e.g.*, 0·5 to 1.5 per cent. by weight of potassium oleate or naphthenate.

The I. G. (Interessen Gemeinschaft)[18] claim the addition to petrol of 40 per cent. of the product distilling below 200°C., produced by the destructive hydrogenation of brown coal to prevent pinking and to allow the engine to be operated at high compression.

A claim is made[19] for the use of metals, *e.g.*, copper, dissolved in methyl-cyclohexanol as an anti-knock. Dr. Sokal[20] coats the inside of the cylinder head first with a silicate binder and then with a mixture of the silicate binder and litharge to prevent pinking.

Several claims are made for the products of cracked oils from low temperature carbonisation and for vapour-phase cracked petrols as non-pinking fuels, but it has been found that the refining necessary to obviate gumming troubles has the effect of reducing their anti-knock value. It would, of course, be possible to largely extend the list of proposals made, and the above have been given as examples of the widely different suggestions made. This all points to the fact that we are still very largely in the dark as to the cause of and the best cure for pinking.

All we can be sure of up to the present is that fuels of the aromatic class, such as benzole and some cracked petrols, do suppress pinking, but have to be used in considerable proportions; this, however, matters less as they are fuels and not inert bodies.

In the analytical edition of the *J. Ind. and Eng. Chem.* for 1929, I, 26, the use of X-Ray apparatus for the quantitative analysis of Ethyl Fluid is described.

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[15] E.P. 277,326.
[16] E.P. 312,245.
[17] E.P. 300,156.
[18] E.P. 259,944.
[19] E.P. 267,079.
[20] *Petr. Times.*, 1928, 1096.

It may be of interest that in June, 1929, the I. G. were reported to have withdrawn "Motalin" (a petrol or benzole-petrol doped with iron carbonyl) from sale, stating that sufficient synthetic petrol of anti-knock value was being produced. This product is sold as Deutsche Benzin in order to show that it is a synthetic motor fuel.

In conclusion one can only say that the two years under review have produced some good work, but that there is yet room for much more to be done.

Benzole.*

By W. H. Coleman, M.I.Min.E., F.I.C. (Member).

The interest that benzole has for the members of the Institution of Petroleum Technologists lies in the fact that, although it is principally a product of the heat treatment of coal and of petroleum, it is not only an excellent motor fuel, when used by itself, chiefly on account of its non-detonating property, but is able to confer this property on other fuels with which it is mixed, and further because it acts as a blending agent when alcohol is used in admixture with petrol or gasoline.

It may perhaps be well to point out that the term "benzole," when used as the name of a motor fuel, includes benzene, toluene and some xylene, and is in fact a mixture of the aromatic or ring hydrocarbons which boil under 150° C., obtained chiefly by the destructive distillation of coal, but also contained in some of the petrols obtained from natural petroleum, especially those from Eastern sources.

During the last two years a good deal of work has been carried out both in the direction of popularising the use of benzole and petrol-benzole mixtures, chiefly the latter, but it has become recognised in both hemispheres as a standard by which the anti-knock value of various petrols and petrol mixtures are rated.

Not only has a great deal of work been carried out in this country by the research chemists of the National Benzole Association and on the Continent by the Benzol Verband in Germany, and the French Association of Benzole Producers "Unibenzols" in France on the improvement of the quality and the increase in the recovery, but others have worked at the conversion of petroleum distillates and natural gas into products of an aromatic nature.

Benzole has been known for many years, but until after the war its chief use was in chemical industry for the production of aniline dyes, explosives and as a solvent, although some was used as a fuel for internal-combustion engines, notably by the Paris Gas Company as well as by private motorists here and abroad.

Benzole for use in the chemical industry is required to be free from paraffins and unsaturated compounds which interfere with the nitration, generally the first step in its use. The consequence of this has been that very drastic methods requiring the use of

* Paper received February 5, 1930.

concentrated sulphuric acid have been adopted for the purification. It has been found that this method of purification removes some of the aromatic as well as certain unsaturated hydrocarbons which are perfectly satisfactory motor fuels, thus causing a lower yield to be obtained than would otherwise be possible. The reason why the before-mentioned method of refining with sulphuric acid has been continued is as follows: some of the unsaturated hydrocarbons, if left in the benzole, polymerise on storage to bodies which tend to form gummy deposits on the inlet valves, inlet valve stems and inlet manifold of internal-combustion engines.

Many attempts have been made to find methods of so treating benzole that the easily polymerisable bodies may be removed without destroying the valuable unsaturated hydrocarbons which will not polymerise and causing the unavoidable loss of a certain proportion of the aromatic hydrocarbons. Among the methods proposed may be mentioned treatment with silica gel, with weaker sulphuric acid both hot and cold, with Fuller's earth (Floridin) in the vapour phase, with mixtures of clay and ferric sulphate, with chlorine, &c., but up to the present the most satisfactory process is that evolved by the Research Staff of the National Benzole Association, which does away with the use of concentrated sulphuric acid and instead adds to the benzole very minute proportions of certain chemicals, a mixture of the three isomeric cresols, commonly known as tri-cresol being very satisfactory. This process, which has been protected in most countries (see E.P. 289,347) gives an increased yield at a very small operating cost.

Beyond the above, there is very little to be written about benzole during the past two years. Some work has been done on the method of estimating aromatics in mixtures, but it must be confessed that up to the present these methods fall short of what might be desired. In Great Britain the production of benzole has increased, and at the present time considerable interest is being taken in the question of benzole recovery from town's gas, at present carried out only in London and at Leeds and at one or two other provincial centres, the bulk of the benzole produced in this country being recovered from the gases from coke ovens.

The popularity of benzole mixture has increased, and its value as a motor fuel is daily being more fully recognised. On the Continent, both Germany and France are alive to its value. In the former country it forms a not inconsiderable proportion of the total motor fuel used, and in France already, in May, 1928, 44 French gas works, in addition to the coke ovens, were recovering benzole, whilst in June of that year it was stated that 80 per cent. of French town's gas was being treated for the recovery of benzole, and that the French production had increased four times since 1921.

At the end of last year an International Conference on Benzole was held in Paris, the chief object of which was to popularise its use and stabilise its quality.

The French Motor Grand-Prix Race is this year, 1930, for the first time to be run on a mixture of benzole and petrol.

Belgium, Holland, Luxemburg, Czecho-Slovakia, Italy and other Continental countries are taking a greater interest in the use of benzole as a motor fuel.

Mention should be made of Dr. F. H. Garner's paper on "The Determination of Aromatics, Olefines, &c., in Petrol[1]," and also Dr. A. B. Manning's paper.[2]

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[1] *J. Inst. Petr. Techn.*, 1928, **14**, 695.
[2] *J.C.S.*, 1929, 1014—1020.